CRITICAL EVALUATION OF A BIOGENIC EMISSION SYSTEM FOR PHOTOCHEMICAL GRID MODELING IN CALIFORNIA

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ABSTRACT

Assessing the relative effectiveness of VOC vs. NO_x control, or simultaneous control of both precursors, in reducing photochemical smog in California's airsheds depends in part on obtaining accurate biogenic emissions inventories. However, while considerable progress has been made in quantifying the contribution of vegetation emissions of VOC many important uncertainties remain. In particular, the biogenic emission inventories prepared for key California airsheds may be based on inappropriate estimates for any or all of the following: biomass and biomass distribution, emission rate assignments, correction factors for diurnal and seasonal influences, and inaccurate coding or methodologies within available emissions models.

The overall objective of this research was to critically and comprehensively evaluate the methodologies and databases with which biogenic hydrocarbon emission inventories are prepared for photochemical modeling in California's airsheds. The results included the following:

- A critical review of biomass databases
- A critical review and update of emission rate databases, algorithms, and methodologies
- Assessment of the utility of remote sensing and aerial imagery technologies for biomass characterization
- A critique of current vegetation emission inventory models
- Identification of gaps in databases, and needed research
- Recommendation of valid protocols for assembling biogenic hydrocarbon emission inventories

Among the most important findings and recommendations were the following. There is a paucity of experimental data for leaf mass constants and other biomass metrics. Similarly, less than 25% of the relevant plant species in California have measured

biogenic hydrocarbon emission rates, and even when such data are available in almost all cases they represent only a single set of environmental and seasonal conditions. Additional measurements are needed and these can be made cost-effectively with guidance from taxonomic relationships. There is an important need to develop canopy correction factors more suitable for California's airsheds. Soil NO_x measurements should be made in regions of high agricultural activity. Validation of biogenic emission inventories and model predictions should be attempted through appropriate ambient air measurements of biogenic hydrocarbons. Remote sensing is unlikely to lead to major advances in the near future in biomass characterization. A detailed evaluation of the four current biogenic emissions models suggests the use of BEIS-2, although GEMAP and VEGIES use input parameters that are more detailed and specific to California. Recommended procedures for assembling and verifying biogenic emissions estimates used in photochemical modeling are presented.

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DISCLAIMER

The statements and conclusions in this report are those of the contractors and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with this material reported herein is not to be construed as either an actual or implied endorsement of such products.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES
(continued)

LIST OF FIGURES

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

ARB	Air Resources Board
ARCINFO	[Vector-format GIS used to provide DRI Landsat TM-based vegetation classification files for the SARMAP/BIOME model]
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
AVHRR	Advanced Very High Resolution Radiometer
BEIS	Biogenic Emission Inventory System (U.S. EPA)
BIOME	Biogenic Model for Emission Estimation (Radian Corporation)
BF_j	leaf biomass factor for vegetation type j
CALVEG	California Vegetation database developed by the California Division of Forestry (from Tanner)
CARB	California Air Resources Board
CDFA	California Department of Food and Agriculture
CDF	California Department of Forestry
CIEE	California Institute of Energy Efficiency
CIR	color infrared
CMB	Chemical Mass Balance receptor model
CO_2	carbon dioxide
DBH	diameter at breast height
DRI	Desert Research Institute
DWR	Department of Water Resources
EF_{ij}	species-specific emission factor for vegetation type j
EPA	Environmental Protection Agency

GC-FID	gas chromatography-flame ionization detection
GC-MS	gas chromatography-mass spectroscopy
GEMAP	Geocoded Emissions Modeling and Projections
GIS	Geographical Information System
IR	infrared
LA	Los Angeles
LAI	leaf area index
LMOS	Lake Michigan Ozone Study
LRT	Long Range Transport
Mt(N) yr^{-1}	megatons nitrogen per year
MTPD	million tons per day
NASA	National Aeronautical and Space Administration
NDVI	normalized difference vegetation index
NMOC	non-methane organic compound
NO_x	oxides of nitrogen (NO + NO_2)
NO	nitrogen monoxide
NO_2	nitrogen dioxide
N_2O	nitrous oxide
OVOC	other volatile organic compounds
PAR	photosynthetically active radiation
PG&E	Pacific Gas and Electric
ppbC	parts per billion carbon

RH	relative humidity
ROG	reactive organic gases
ROM	Regional Oxidant Model
SAB	Sacramento Air Basin
SAI	Systems Application International
SARMAP	SJVAB/AUSPEX Regional Modeling Adaptation Project
SCAQMD	South Coast Air Quality Management District
SCAQMP	South Coast Air Quality Management Plan
SJV	San Joaquin Valley
SJVAB	San Joaquin Valley Air Basin
SJVAQS	San Joaquin Valley Air Quality Study
SoCAB	South Coast Air Basin
SO_x	oxides of sulfur (SO_2 + SO_3)
TM	Thematic Mapper (NASA Landsat satellite instrument)
TPD	tons per day
UAM	Urban Airshed Model
UCR	University of California, Riverside
USFS	United States Forest Service
USGS	United States Geological Survey
UTZ	urban terrain zone
VEGIES	Vegetation Emission Inventory System
VOC	volatile organic compound

1.0 EXECUTIVE SUMMARY

1.1 Introduction and Background

Extensive and effective emission control strategies by the California Air Resources Board (ARB) and the South Coast Air Quality Management District (SCAQMD) have led to a remarkable reduction over the past fifteen years in peak ozone levels, as well as in the numbers of first and second stage episodes, in California's South Coast Air Basin (SoCAB). Unfortunately, however, the SoCAB and several other major regions of the state (e.g. the Central Valley) continue to experience serious air quality problems (SCAQMP 1994).

The National Research Council (NRC, 1991), addressing the difficulties in further reducing photochemical smog, noted that both regional and national inventories of hydrocarbon emissions from vegetation are not well understood (NRC, 1991). However, experimental and modeling studies have demonstrated that biogenic hydrocarbons can constitute a significant contribution to the overall volatile organic compound (VOC) inventory in both urban and rural regions and on average biogenic hydrocarbons are 2-3 times more reactive than emissions from mobile sources.

Recent modeling studies by the ARB have also indicated that development of specific emissions control strategies for reducing ambient ozone concentrations in some areas of California are dependent upon estimated fluxes of biogenic hydrocarbons. These studies showed that emissions of hydrocarbons from vegetation can make the difference between oxides of nitrogen (NO_x) emission controls or ROG emission controls being the most effective in reducing ozone concentrations. Not surprisingly, modeling studies performed for other areas of California showed that vegetative hydrocarbon emission estimates become increasingly important as anthropogenic hydrocarbon levels are reduced in response to implemented and proposed control strategies.

However, analyses of model simulation results in some cases have also suggested that emission inventories for biogenic hydrocarbons may be too high, or that there are other problems in the methodology being employed to evaluate the relative importance of vegetative emissions. These results suggested the possibility that biogenic emissions

estimates prepared for California for use in photochemical modeling studies may be based on inappropriate estimates of any or all of the following: biomass and biomass distribution, emission factors, correction factors for diurnal and seasonal influences, and/or inaccurate coding within the available emissions models. The present project was designed to critically evaluate these and other key factors involved in assembling reliable biogenic emission inventories and models, identify important data gaps, and recommend a state-of-the-art protocol for biogenic emission inventory development.

1.2 Overall and Specific Objectives of this Project

The overall objective of this project was to critically and comprehensively evaluate the processes and databases with which biogenic emission inventories have been prepared for photochemical modeling in California, including those prepared for the South Coast and San Joaquin Valley Air Basins.

The specific objectives were to:

- Critically review and update currently available vegetative emission inventory biomass databases developed for photochemical modeling studies in California.

- Review emission rate factors used for vegetative species in California and update their database to reflect California's specific conditions. This review included assessments of the biochemistry and physiology of biogenic hydrocarbon production and emission, the spectrum of speciated biogenic VOC's emitted by vegetation, emissions of oxides of nitrogen from soil, and a review of the development of algorithms used to estimate emissions under different environmental conditions.

- Review the availability and application of satellite imagery and aircraft photography for the development of biomass estimates for input to emissions models.

- Review currently available vegetative emission inventory models used to develop hourly, gridded emission estimates, recommend the best methods and models to incorporate into an overall vegetative emission estimation system for California, and determine which factors need to be updated for an accurate representation of the range of growing conditions in California.

- Identify specific information, gaps in databases, and areas of methodologies which require further research or data acquisition.

- Recommend procedures for verifying biogenic emission estimates used in photochemical models.

The remainder of this report describes the methods employed and results obtained for each of these tasks.

1.3 Critical Review of Biomass Estimations for the California South Coast Air Basin and the San Joaquin Valley Air Basin

Knowledge of biomass, both plant species distribution and quantification of green-leaf mass, is essential in assembling reliable biogenic emission inventories since plant species differ in amount of leaf mass, leaf mass per unit volume and emission rate per unit leaf mass. Unfortunately, few biomass constants have been experimentally determined to date, and error estimations for biomass calculations in California airsheds have apparently not been made. For naturally vegetated regions within California airsheds, the error of calculation of biomass for each species could be expected to be at the high end of the 15-30% range and likely greater than 30% due to the high degree of endemism of the flora. Because of the labor and expense associated with field mapping of natural plant communities, historic documents such as the vegetation surveys made in the 1930's are still being used, despite their not reflecting changing land-use patterns and plant species distribution over many decades.

In this study, four investigations were critically reviewed with the goals of obtaining current perspective on the state of knowledge, evaluating the methods utilized, assessing uncertainties and identifying areas where further research is necessary. The general approach taken in these studies was that of building a biomass inventory from the bottom up, consistent with the known requirements linking the flux of biogenic emissions to the amount of foliage per species. The stratified random sampling approach for inventory development in the urban areas of the SoCAB appeared to be a reasonably sound and practical method of executing the estimation.

Quantitative estimates of biomass appeared reasonable for the SoCAB; however, because of differences in study area and data presentation it was difficult to quantitatively compare the work of Winer and co-workers (Winer *et al.*, 1983; Miller and Winer, 1984)

to that of Horie *et al.* (1990). Also, because of the normal onshore flow, it is arguable whether plants in the far eastern portions of the SoCAB, especially in the Coachella Valley and high desert areas should be considered as "source" areas for photochemical smog in the SoCAB.

The inventory for the urban areas within the SJVAB appeared to be adequate. Biomass within the SJVAB is found mostly in agricultural and natural settings. Refinement is needed for both. For agricultural areas within the SJVAB, a direct approach based on current-year CDFA data is recommended rather than the more circuitous route based on remote sensing. It is doubtful that remote sensing of agricultural areas can provide a better estimate in the near future than the actual inventories available of crops and acreage. Development within CDFA toward listing of crops on a geographical grid system further recommends this data source for possible compatibility with GIS databases.

For natural communities, further characterization of plant species distribution and/or community distribution and composition is needed. In particular, California state cooperative vegetation type maps and CALVEG should be validated, for example through selective ground survey. It is unlikely remote sensing alone can provide the level of detail necessary for an accurate biomass inventory. However, if the existing maps or database are found to be reasonably accurate, remote sensing could be used to identify and quantify future changes. It should be noted there is progress toward a standardized classification scheme for plant communities (Keeler-Wolf, 1995). The Ecological Society of America has a subcommittee to address vegetation standards and classification and standardized classification scheme for California is expected in print in late 1995, distributed by the California Native Plant Society.

Finally, where necessary (e.g. for dominant plant species), biomass constants should be determined in the field for urban, ornamental, agricultural crops, and plants within the natural community.

1.4 Critical Review of Biogenic Emission Factor Development and Compilation

The purpose of this assessment was to evaluate the current state of knowledge concerning the emission of biogenic NMOC's from plants, how those emission rates are measured, the chemical composition of such emissions, and the effect of environmental factors on emission rates.

Composition of Biogenic NMOC Emissions. The particular distribution of organic compounds emitted from different vegetation types depends on the specific characteristics of each individual plant species and can vary widely. Table 1-1 lists approximately 50 different NMOC species identified as being emitted from approximately 30 ornamental, agricultural and natural plant species found in the San Joaquin Valley in California. However, only a limited number of compounds generally dominate emissions on a mass basis, and compounds other than isoprene and the terpenoids have been found to constitute only a minor portion of total NMOC emissions from many plant species. However, additional investigation is needed to more fully characterize the speciated composition of NMOC emissions from vegetation.

Emission Variability Due to Environmental Conditions. The most influential environmental parameter controlling monoterpene emission rate is temperature, while light intensity does not directly influence the emission rates of these compounds.

Seasonal variations in emission rates have been demonstrated in a number of plant species. Studies of Valencia orange trees showed emissions of linalool were a factor of ten higher during the blossoming season as compared to the average annual emissions outside this season (Arey *et al.*, 1991c). Emissions of α-pinene from *Pinus densiflora* were found to be lower in winter than would be expected based only on decreased temperatures as compared to summertime emissions. Similar seasonal variations were observed for other species including red oak (Flyckt, 1980), English oak (Dilts *et al.*, 1990) and forested regions (Isodorov *et al.*, 1985).

In contrast to monoterpene emission, isoprene emission is well correlated with photosynthesis. Numerous hypothesis have been presented to account for observed isoprene emission rates under a wide variety of conditions, however, complete elucidation of the control mechanisms has yet to be achieved, although in a recent report, Sharkey

Table 1-1. Compounds identified as emissions from agricultural and natural plant species (from Winer *et al.*, 1992)

Isoprene

MONOTERPENES
- Camphene
- 2-Carene
- Δ^3-Carene
- Limonene
- Myrcene
- cis-Ocimene
- trans-Ocimene
- α-Phellandrene
- β-Phellandrene
- α-Pinene
- β-Pinene
- Sabinene
- α-Terpenine
- γ-Terpenine
- Terpinoline
- Tricylene or α-thujene (tentative)[b]

SESQUITERPENES
- β-Caryophyllene
- Cyperene
- α-Humulene
- Other Isomers[c]

ALCOHOLS
- *p*-Cymen-8-ol (tentative)[b]
- cis-3-Hexen-1-ol
- Linalool

ACETATES
- Bornylacetate
- Butylacetate (tentative)[b]
- cis-3-Hexenylacetate

ALDEHYDES
- *n*-Hexanal
- trans-2-Hexanal

KETONES
- 2-Heptanone
- 2-Methyl-6-methylene-1,7-octadiene-3-one (tentative)[b]
- Pinocarvone (tentative)[b]
- Verbenone (tentative)[b]

ETHERS
- 1,8-Cineole
- *p*-Dimethoxybenzene (tentative)[b]
- Estragole (tentative)[b]
- *p*-methylanisole (tentative)[b]

ESTERS
- Methylsalicylate (tentative)[b]

n-ALKANES
- *n*-Hexane
- C_{10}-C_{17}

ALKENES
- 1-Decene
- 1-Dodecene
- 1-Hexadecene (tentative)[b]
- *p*-Mentha-1,3,8-triene (tentative)[b]
- 1-Pentadecene (tentative)[b]
- 1-Tetradecene

AROMATICS
- *p*-Cymene

[a]Unless labeled "tentative", identifications were made on the basis of matching full mass spectra and retention times with authentic standards.

[b]Tentative identifications were made on the basis of matching the mass spectra (and retention order when available) with published spectra (EPA/NIH Mass Spectral Data Base, and/or Adams, 1989).

[c]Several additional compounds were observed which can be assigned as $C_{15}H_{24}$ sesquiterpenes based upon their mass spectra and apparent molecular ions at *m/z* 204.

and Loreto (1995) propose that the role of isoprene synthesis and emission is to provide thermal tolerance.

Although isoprene emissions have been found to be affected by light intensity, temperature, relative humidity, ambient CO_2 levels, water stress, and nutrient availability (see reviews by Sanadze, 1991; Sharkey *et al.*, 1991; and Monson *et al.*, 1991a), light intensity and temperature are believed to have the greatest effect on emission rates. As a result, isoprene emission is observed primarily during daylight hours, with nighttime emissions being two orders of magnitude lower than daytime emissions. Over short periods of time, isoprene emission can increase as much as tenfold with a 10 °C increase in leaf temperature (Sharkey and Loreto, 1993).

Little work has been published to date concerning seasonal variations in isoprene emission rate, and further investigations are needed to establish whether such variations have any significant influence on the total isoprene emission inventory for a given airshed.

In summary, isoprene, monoterpenes, sesquiterpenes, and oxygenated biogenic VOC emissions exhibit wide variations both between and among different plant species due to biochemical and morphological differences, environmental conditions, and diurnal and seasonal variations. Knowledge of how these parameters affect emission rates is essential in making more accurate predictions concerning biogenic emission rates and therefore these factors deserve greater attention. At the present time, a number of these parameters are not considered when applying numerical computer models for estimating total VOC emission inventories which may lead to inaccurate estimates of total biogenic emissions at different times of the day or year. Clearly, further research is needed to obtain a better understanding of the factors which regulate such emissions in order to achieve more reliable estimates of their influence on regional and global air quality.

Experimental Methodologies for Determination of Biogenic Emission Factors. Both chamber and ambient atmosphere measurements (which includes tracer studies and micrometeorological gradient profiles) have been employed to measure emission rates of biogenic NMOC's. A critical review has been conducted to identify the advantages and disadvantages unique to each approach and recommendations are given later in this section.

Assignment of Emission Rates to Non-Measured Plant Species. Of the more than 400 plant species currently identified in the SoCAB (Horie *et al.*, 1990), experimental emission rate measurements have been performed on only about twenty percent and there exists a need to develop methodologies for assigning emission rates to those plant species for which no measured data are available. Benjamin *et al.* (1995b) described such a methodology based on taxonomic relationships at the genus and family level, and Horie *et al.* (1991) used a similar procedure to assign emission rates to non-measured species.

At the present time, taxonomic relationships appear to provide both a cost- and time-effective method for assigning emission rates to non-measured plant species given the lack of direct measurements of hydrocarbon emissions for many plant species found in California's air basins. However, the strengths and limitations of this methodology needs to be recognized. Benjamin *et al.* (1995b) found that most tree species within the same genus exhibited emission rates which differed by a factor of ten or less. While many tree species within the same family also exhibited emissions which differed by less than a factor of ten, emission rates for species within the family *Arecaceae*, for example, differed by as much as a factor of thirty-two, indicating that family level assignment of emission rates involves a greater level of uncertainty.

On the other hand, given that emission rates across all families listed in the study varied by over four orders of magnitude, the taxonomic approach appears to provide a satisfactory first order approximation of NMOC emission rates. However, as noted by Benjamin *et al.* (1995b), the reliability of the taxonomic method for assigning emission rates to non-measured plant species can be improved by performing additional emission rate measurements, especially on plant species from families and genus' in which few measurements have been performed to date. Another recommendation is that future direct measurements be performed on those plant species with the largest biomasses in a given airshed and those which have either very high or very low emission rates assigned on the basis of the taxonomic method. This would not only provide additional data which can be used to obtain greater reliability in further application of the taxonomic method, but will also reduce overall uncertainties in the generation of future biogenic emission inventories.

Algorithms for Emission Rate Variability. In order to normalize emission rates to common conditions (e.g. standard temperature), and to use numerical computer models to evaluate the influence of vegetation on ambient air quality, algorithms have been developed to describe variations in hydrocarbon emissions by vegetation as a function of these environmental parameters. These algorithms have evolved over the past 15 years due to improved knowledge of the influence of environmental conditions on emission rates, and from emission measurements for an increasing number of plant species. As a result of this evolution, biogenic emission inventories compiled over this 15 year time period may include different emission rates for a given vegetation species, even for the same set of environmental conditions. A critical review of the algorithms used for isoprene and monoterpene emissions is presented in Section 4.8. The recommended approach for adjusting isoprene emissions for environmental conditions is to use the Guenther *et al.* (1993) algorithm to normalize emission rates from raw data when available, and to use the normalized emission rates as corrected by the Tingey *et al.* (1979) or Pierce *et al.* (1990) algorithms from earlier studies when the raw data were not given. The Guenther *et al.* (1993) algorithm for monoterpene compounds is also recommended.

Leaf Canopy Correction. The use of canopy models to correct for variations in environmental conditions at various heights within leaf canopies are viewed as important advancements in the characterization and quantification of biogenic hydrocarbon emission rates. However, their applicability to the SJVAB and SoCAB, as well as many other airsheds in California, is questionable. While the attenuation of solar radiation within various vegetative communities needs to be accounted for, the characteristics of these California land use regions are quite different from those for which the canopy models were developed and applied. Specifically, the models have been developed and applied to homogeneous forest communities with species compositions consisting of only a few types of trees. This is not the case in either the SJVAB or the SoCAB where the plant communities are much more diverse. Clearly, there are both a much greater number of plant types and more complex community structure in these air basins. As a result, the effects of shading on isoprene emission rates from different plant species within these

regions may not be accurately predicted by current canopy models developed for southern, northeast and northwest forests. Secondly, the plant densities in many of the vegetative communities in the SJVAB and SoCAB are not as high as in the regions for which the models were developed. As a result, significantly more leaf biomass will be subject to direct sunlight in these airsheds than in forest communities.

Improved methodologies need to be developed to account for canopy shading effects in the vegetation communities found in California. At present, the SCAQMD's reduction factor of 23% remains the best approach for the plant species distributions found in these airsheds, while recognizing this is a simplistic approximation. Clearly, further investigation is needed to determine the appropriateness of these algorithms and correction factors for use in California's air basins in order to reduce the level of uncertainty biogenic emission inventory estimates.

NO_x Emissions from Soils. While most biogenic emission inventories have focused on NMOC emissions, until recently little attention has been paid to biogenic sources of NO_x. However, recent evidence suggests NO_x (primarily as NO) emissions from soils have been underestimated in the past and therefore may play a significant role in local, regional, and global NO_x budgets. Although NO_x emissions from soils in urban regions are likely to be small or negligible in comparison to anthropogenic emissions of NO_x, the relative contribution of soil NO_x emissions in agricultural and rural regions may be significant due to lower levels of NO_x from combustion sources in such regions. Therefore, soil NO_x emissions in agricultural and rural regions could have implications concerning possible control strategies designed to limit ozone levels in such regions.

A number of studies have been performed measuring NO_x emission rates from a variety of different soil types from different regions of the world. Agricultural fields and grasslands appear to have the highest emissions. It is recommended that for rural and agricultural areas NO_x emissions from soils should be included in modeling efforts to determine the effect of biogenic emissions on ambient air quality.

Critical Review of Inventories Relevant to California Air Basins. A critical review of the three principal biogenic hydrocarbon emission inventories developed for California airsheds is provided in Section 4.10.

1.5 Remote Sensing Applications for Biomass Identification and Quantitative Estimation

A detailed and comprehensive review of remote sensing techniques and their potential application to characterize biomass is given in Section 5.0. Rapid development of remote sensing technology has occurred, fueled by interest in satellite-based systems, instrumentation and the computer capability to handle large volumes of data. Image enhancement and classification techniques continue to improve. Currently, remote sensing from satellite platforms offers the capability of determining land cover classes where spectral characteristics are well-defined and distinct. However, establishment of plant identity at the species level goes beyond the normal requests made of even advanced instrumentation.

Remote sensing is useful for identifying individual plant species where differences are obvious in terms of spectral characteristics or phenology. Because of the similarity of plant components, species identification in ecosystems is limited to situations where choice can be made among plant types, implying a priori knowledge exists. Biomass may be adjusted using remote sensing and the NDVI, but quantitative baseline values for biomass are needed from some other source. AVHRR data for quantifying cover estimation are most useful for large areas of homogeneous vegetation. California airsheds pose problems for remote sensing because of the variety of plant communities and breadth of transition zones, although aerial photography remains a useful technology where fine resolution is required.

Plant biophysical properties as inferred from chlorophyll content and water content are amenable to remote sensing. Unfortunately, no direct link shared among many plant species has been discovered between a measurable biophysical property and emission rate.

GIS maps or databases should contain a clear history of development, including criteria for classification and method of classification. Quantitative error estimation is possible, and recommended.

1.6 Critical Review and Evaluation of Biogenic Emission Inventory Models

The four most widely-used biogenic emission modeling systems: BEIS (PC-BEIS and UAM-BEIS), BEIS-2, VEGIES, and GEMAP were critically reviewed (see Section 6.0 for comprehensive discussion). These models all predict biogenic hydrocarbon emissions by multiplying the following four parameters for each species and summing the species emissions:

- Area covered by specific species
- Leaf biomass factor for specific species
- Emission factor for specific species
- Species-specific environmental adjustment factor

Table 1-2 summarizes the methods used by each of these models for parameter estimation. The table also lists the minimum estimated uncertainty factor for each parameter based on qualitative assessments for each parameter. The estimated minimum uncertainties are as much as a factor of 2 in the formulas applied by the emission models to predict VOC leaf biomass, plant specific VOC emission factors, VOC environmental factors, and soil NO_x emissions.

Our analysis of the appropriateness of each of the models for use in modeling biogenic hydrocarbon emissions in California has yielded the following observations for each of the models:

BEIS and BEIS-2

- BEIS and BEIS-2 do not adequately represent land-use type in California.
- BEIS and BEIS-2 emission factors are based primarily on measurements made in the eastern United States and may not be representative of emissions of similar species in California.
- BEIS-2 is the only model to use the most recently developed environmental correction algorithm, which has been shown to be more accurate than the algorithm used in the other models. However, a small coding error in the application of these formulas was found and needs to be corrected.

Table 1-2. Features of the biogenic models reviewed.

Model	Land-Use Coverage	Leaf Biomass	Vegetation Specific Emission Factors	Environmental Factor	Biogenic NO_x Model
BEIS	Geocology	Lamb et al., 1987	Lamb et al., 1987	Tingey et al., 1979, 1980	NO
UAM-BEIS	Geocology	Lamb et al., 1987	Lamb et al., 1987	Tingey et al., 1979, 1980	YES
GEMAP	Satellite imagery, USGS land use	Sidawi and Horie, 1992	Sidawi and Horie, 1992	Tingey et al., 1979, 1980	NO
VEGIES	N/A	N/A	Causley and Wilson, 1994	Tingey et al., 1979, 1980[a]	NO
BEIS-2	U.S. Forest Service, AVHRR	Guenther et al., 1995	Guenther et al., 1995	Guenther et al., 1991, 1993	YES
Estimated minimum uncertainty factor	No estimate	2	2	2.4	2[b]

[a] Includes a physically incorrect diurnal adjustment factor for monoterpenes.
[b] Based on differences in UAM-BEIS and BEIS-2 NO_x environmental factors.
N/A = Not available.

- PC-BEIS and UAM-BEIS leaf models produce some unusual results.
- BEIS-2 was the most robust and easily followed code.

GEMAP

- Applies emissions and biomass factors that are specific to the AUSPEX region.
- Applies the most extensive land-use coverage.
- Uses an outdated environmental correction factor algorithm.
- Does not have a soil NO_x module.

VEGIES

- Applies emission and biomass factors that are specific to the SCAQMD.
- Applies a physically incorrect solar radiation adjustment to monoterpene emissions.
- Does not adjust leaf temperature for canopy effects.
- Uses an outdated environmental correction factor algorithm.
- Does not have a soil NO_x module.

Given these observations, we can make several recommendations on what aspects of each model can be used to develop a state-of-the-art model that is optimized for use in California.

Leaf biomass factors and species-specific emission factors are best represented by the GEMAP model for the AUSPEX region and the VEGIES model in the SoCAB. The BEIS-2 model has significantly fewer leaf biomass and species-specific emission factors, and the emphasis in BEIS-2 is primarily on the eastern United States where emission factors may be different than in California. Thus, GEMAP and VEGIES provide both the most comprehensive data base of leaf biomass factors and species-specific emission factors that are most applicable in California.

The environmental correction model proposed by Guenther *et al.* (1991) has been shown to agree better with existing observation than the earlier models of Tingey *et al.* (1979, 1980). At the time of this report, the Guenther algorithm is presently only

incorporated into the BEIS-2 model, while the others still use the Tingey algorithm. None use the most recent algorithms by Guenther *et al.* (1993) which we recommend (see Section 4.0)

Although it was not the focus of this study, we have briefly reviewed the literature on biogenic soil NO_x, and have determined that while there are currently large uncertainties in soil NO_x emission estimates, present estimates suggest the need for their inclusion into UAM, and for further chamber and laboratory studies. Only BEIS-2 and UAM-BEIS contain soil NO_x models. The estimation methods in both models are similar except that BEIS-2 used more crop-specific data on agriculture for its emission estimates. As agriculture is particularly important in California, the BEIS-2 model is likely to produce better estimates of soil NO_x.

Recommendations. Overall, BEIS-2 is currently the best biogenic emissions model available. It incorporates the most recent advances in environmental adjustments and has a soil NO_x module. It is also has the most robust and easily followed code. However, GEMAP and VEGIES use input parameters that are more detailed and more specific to California than those used in BEIS-2. Fortunately, BEIS-2 can be modified to account for California-specific leaf biomass factors and species-specific emission factors, or GEMAP could be modified to incorporate the improvements of BEIS-2, including the addition of a biogenic soil NO_x module. If BEIS-2 is selected as the platform for California's biogenic model, we recommend that the area of vegetation types, the leaf biomass factors, and the species-specific emission factors used in GEMAP and VEGIES, plus supplements for the remainder of California, be incorporated. Some features of UAM-BEIS should also be added into BEIS-2 to allow for direct use in UAM.

1.7 Data Deficiencies and Future Research Needs

While considerable progress has been made in quantifying the contribution of vegetation emissions of reactive organic gases in terms of identity, quantity, and reactivity, it is also apparent that many uncertainties remain, which must be addressed by further research. Here we suggest research most likely to resolve key uncertainties, in a cost-

effective manner, and suggest priorities among current significant deficiencies in needed data, methodologies, or models.

Emission Rate Measurements. A systematic experimental programs of emission rate measurements is needed for selected plant species which have not yet been investigated, with an emphasis on the most important species in California. Of the more than 500 plant species identified in the SoCAB and in other California airsheds, to date the biogenic hydrocarbon emissions of only about 125 have been measured. Fortunately, it may not be necessary to conduct measurements for all remaining species. Rather, taxonomic relationships and biomass considerations can be exploited to prioritize plant species for study. For example, plant species which have been assigned either high emission rates or zero emission rates, based on taxonomic relationships, should be given highest priority, both in order to reduce the current level of uncertainty in emissions inventories, and to further test and validate taxonomic predictions. Similarly, plant species which comprise a large fraction of biomass or occupy extensive ground area should be given priority attention. The taxonomic methods developed by Benjamin *et al.* (1995) provide a basis for developing cost-effective criteria for choosing which plant species should be selected for future experimental studies. Generation of additional emission rate data for the most critical plant species in California's airsheds remains the most urgent research priority.

Ideally, emission rate measurements should be performed on a range of leaves, branches, and whole plants for a given plant species in order to develop a better understanding of the range of rates from that plant species. Further, if possible, emission rate measurements should be performed at various times of the year, or at least from early spring to late fall, to characterize any seasonal variations in emissions. Although a number of plant species have been shown to exhibit seasonal variation in emissions, to date most reported emission rates were obtained over a very limited time period (e.g. one day). It should be recognized that these more extensive investigations may be beyond current research resources, and should be assigned a secondary priority. However, additional comparisons should be made between emission rate measurements using the

enclosure method and measurements made with leaf cuvettes, a technique which could expedite gathering of emission rate data with accurate light intensity data.

Atmospheric Transformations. Although rate constants are available for the reaction of isoprene and most of the important monoterpenes with OH and NO_3 radicals and ozone, additional kinetic data are required for the sesquiterpenes and other compounds identified as emissions from vegetation. While the mechanism of reaction of isoprene with the OH radical has been well established, this is not true for mono- and sesquiterpenes. Further investigation concerning mechanisms of reaction of such NMOC's needs to be performed, especially for compounds such as alpha- and beta-pinene, d-limonene, myrcene, and sabinene which are prominent emissions from a variety of plant species. Such studies of reaction mechanisms are required not only for OH radical reactions but also for reaction with NO_3 radicals and ozone. In addition to further investigations of the reaction mechanisms of parent compounds, the atmospheric fate of the secondary products produced by their reactions needs to be established, including not only chemical reaction pathways, but also wet and dry deposition rates and gas-to-particle formation processes.

To date, maximum incremental reactivities have been reported to only for isoprene and α- and β-pinene. Further investigation is needed of the ozone-forming potential of additional important monoterpenes and other biogenic hydrocarbons.

Improved Emission Algorithms. At the present time, the most accurate emission rate algorithm is based on experimental data from only four plant species. Assessments of the environmental influences on emission rates is needed for additional plant species in order to improve the reliability of the present algorithms. These studies would most properly be conducted by those research groups which have specialized in the development of emission rate algorithms, and be supported by agencies other than the ARB.

Improved Canopy Correction Algorithms. Further investigation is required to develop improved canopy correction, or leaf shading, factors suitable for California's air basins. In particular, new canopy correction algorithms need to be developed, or existing algorithms validated, for the SoCAB and SJVAB, since the isolated or widely separated

urban trees in these airsheds are not likely to be well modeled by current forest canopy correction algorithms. Similarly, the canopy correction factor developed by the SCAQMD, a blanket 23% reduction in emissions, is simplistic and may not represent actual emission reductions due to shading effects. Given the linear impact of such canopy correction factors on total emission inventories, the development of more applicable and reliable canopy algorithms is a high priority.

Validation of Compiled Biogenic Emission Inventories. Validation of compiled biogenic emission inventories for a variety of vegetative communities needs to be performed. One approach would involve comparing ambient air biogenic VOC measurements, utilizing grab sample, gradient, or tracer methodologies, with predictions from airshed models incorporating biogenic emissions inventories appropriate to a given airshed. Clearly, this is a difficult challenge given the complexity of the vegetative communities present, for example, in the SoCAB and SJVAB, and given the high photochemical reactivity of isoprene and the monoterpenes. The air quality study scheduled for the SoCAB in 1997 offers an opportunity to collect ambient air data for biogenic hydrocarbons which might be used to conduct such a validation.

Emissions inventories of NO_x compounds from soils need to be compiled in order to determine their contribution to the total NO_x budget, especially in the SJVAB with its extensive agricultural activities. Chamber studies should be coupled with atmospheric measurements to obtain a reliable understanding of NO_x fluxes from agricultural fields. We recommend such research be supported in California.

Quantitative Comparison of Emissions Models. Further development of biogenic emissions models is currently the subject of intensive research at the Federal level. Since each of the models reviewed in this study was judged to have desirable attributes, a more quantitative comparison between the existing models would be helpful in identifying key differences and strengths and weaknesses. This would involve running each model for a common set of inputs and comparing the results. In addition, a sensitivity analysis could be performed on input parameters, such as leaf biomass factors and species-specific emission rates, using the ranges of values reported in the literature for these parameters.

Although the environmental adjustment algorithms in BEIS-2 are generally superior to the algorithms in BEIS, it is important to note that BEIS-2 does not currently use a leaf energy model. The ARB should consider adding a replacement leaf energy model.

BEIS-2 and UAM-BEIS contain a biogenic soil NO_x emission model; PC-BEIS, VEGIES, and GEMAP do not have such a model. We recommend that BEIS-2 be run with nitrogen fertilizer application data for the Central Valley of California to estimate the soil NO_x emission rates.

Linkage of Remote Sensing to Emission Rates. Plant biophysical properties as inferred from chlorophyll content and water content are amenable to remote sensing. Unfortunately, no direct link shared among many plant species has been discovered between a measurable biophysical property and emission rate. Because of the enormous potential value of such a link, research is needed to explore whether such a link exists. However, no obvious experimental approach appears available at this time, and this is not judged appropriate research for support by ARB relative to other priorities identified in this study.

Validation of Plant Maps or Databases. For natural communities, further characterization of plant species distribution and/or community distribution and composition is needed. In particular, either California state cooperative vegetation type maps or CALVEG could be validated, for example through selective ground survey. Because CALVEG appears to be the only current GIS database for the SJVAB, validation through field studies is recommended. Given the direct importance of plant species and biomass distribution in compiling emission inventories, this is judged to be a high priority.

Biomass Constants. At present, there is a paucity of experimentally determined leaf mass constants for California plant species. Biomass constants should be determined in the field for key agricultural crops and for plants commonly found within the natural communities of the SoCAB and SJVAB. The highest priority plants in the SJVAB include agricultural crops occupying large acreages, such as cotton, almonds, and table grapes. Biomass constants are relatively easy to determine experimentally, and actual measurement is preferred rather than extrapolation or interpolation from plant data in the

literature. Acquisition of these data for key plant species is a high priority relative to other data deficiencies identified here.

1.8 Recommended Procedures for Verifying Biogenic Emission Estimates Used in Photochemical Models.

The intent of this section is to provide guidance to the ARB and ARB-supported researchers in assembling more reliable biogenic emission inventories for California's airsheds, and in the use of such inventories in photochemical models. The protocol recommendations given here arise from the critical review conducted in this report of past and present practices in each step necessary in generating such inventories and in applying them in airshed models. In certain cases, where current practices are still deemed insufficient to achieve a higher level of reliability in biogenic emission inventories, we recommend enhanced procedures which will require a commensurate commitment of resources.

Emission Rate Measurements. Emission rate measurements should be performed using a flow-through plant enclosure apparatus as described by Arey *et al.* (1991a,b,c, 1995) and Winer *et al.* (1989, 1992). In this method, a Teflon bag supported on a PVC-pipe frame is placed over a whole plant or a portion of the plant and medical breathing air containing ambient humidity and CO_2 levels is flowed through the chamber at a rate of approximately 40 L min^{-1}. Air flow should be continued for at least three air exchanges prior to sampling to ensure that steady-state NMOC concentrations in the chamber are achieved. Chamber air sampling should then be performed using adsorbent cartridges for hydrocarbon analysis by GC-FID and/or GC-MS analysis. This methodology is preferred over the static chamber enclosure method as described by Zimmerman (1979) because of fewer problems associated with rough handling, and the larger chamber volumes which avoid sharp increases in temperature and humidity levels. However, it should be emphasized that even with a rigid enclosure apparatus great care must be taken to minimize plant specimen disturbance. Further research may indicate that a leaf cuvette technique can be used effectively for isoprene emission rate measurements.

Emission rate measurements should be performed under conditions which approximate prevailing environmental conditions found in the airshed of interest. All relevant physical parameters, including temperature, light intensity levels, CO_2 and humidity levels, should be reported with the observed emission rates, not only to permit future evaluation of the effects these factors have on emission rates, but to permit normalization to standard environmental conditions as improved emission rate algorithms are developed. This is especially true for agricultural species where the dependencies on environmental effects have not yet been fully established. In addition, the calculations used in deriving emission rates from these measurement data should be explicitly given.

The apparent water status of a plant (e.g. well-irrigated vs. summer drought conditions) and its nutrient status should be noted based on visual observation. If future research finds a strong correlation between emission rate and water status or specific nutrient levels, these factors will need to be measured and reported more precisely.

Ideally, emission rate measurements should attempt to include analysis for all major NMOC's emitted from each individual plant and these should be reported individually. Emitted compounds should not be compiled into broad classification types (e.g. monoterpenes) for reporting purposes. If classification of NMOC species into groups is needed, this should be done according to reactivity and/or ozone-forming potential rather than compound structural class.

Based on difficulties we encountered in attempting to critically evaluate reported emission rate data, it is essential in the future that researchers report, or make available on request, the underlying emission rate data obtained in experimental programs, as well as the data on the corresponding environmental conditions. This would permit future retroactive correction for environmental conditions such as light intensity and temperature as new correction algorithms become available. At the same time, investigators should make explicit in reports and journal articles how emission factors they report are derived from present algorithms. Finally, whenever possible, data concerning leaf-to-leaf and plant-to-plant variability in emission rates should be reported, in order to further characterize the range of uncertainties in the reported measurements.

Models. Overall, BEIS-2 is currently the most appropriate biogenic emissions model since it incorporates the most recent advances in environmental adjustment factors and contains a soil NO_x module. It also comprises of the most well documented and easily followed code. However, GEMAP and VEGIES use input parameters that are more detailed and more specific to California than those used in BEIS-2. Fortunately, BEIS-2 can be modified to account for California-specific leaf biomass factors and species-specific emission factors. Alternatively, GEMAP could be modified to incorporate the improvements of BEIS-2, including the addition of a biogenic soil NO_x module.

If BEIS-2 is selected as the platform for California's biogenic model, we recommend the area of vegetation types, the leaf biomass factors, and the species-specific emission factors used in GEMAP and VEGIES, plus supplements for other California airsheds, be incorporated. Some features of UAM-BEIS should also be added to BEIS-2 to allow for direct use in UAM.

We also recommend that any California biogenic emission modeling system include an uncertainty module which would allow the model to generate a range of reasonable (best estimate, high, low) biogenic emissions as inputs to an air quality model. In this way, optimal anthropogenic emission reduction scenarios for a range of biogenic emissions could be developed.

Biomass Inventories. The stratified random sampling approach for inventory development in the urban areas appears to be a reasonably sound and practical method for estimating biomass. The data developed by Horie *et al.* (1991) and Winer *et al.* (1983) for the SoCAB appear to adequately represent urban vegetation in that airshed. Similarly, the inventory developed by Sidawi and Horie (1992) for the urban areas within the SJVAB appear to be adequate and may be used in emissions calculations. However, the importance of conducting adequate ground surveys to validate imagery-based assessments cannot be overemphasized.

For agricultural areas within the SJVAB, a census approach based on recent CDFA data is recommended rather than an approach based on remote sensing. It is doubtful that in the near future remote sensing of agricultural areas can provide a better estimate than the actual inventories available of crops and acreage. Movement within CDFA toward

listing of crops on a geographical grid system further supports the choice of this data source for possible compatibility with GIS databases.

For the natural areas, it should be noted there is progress toward a standardized classification scheme for plant communities (Keeler-Wolf, 1995). The Ecological Society of America has a subcommittee addressing vegetation standards and classification. A standardized classification scheme for California is expected to be published in late 1995, and distributed by the California Native Plant Society. This standardized scheme should be used to define and discuss plant communities. Biomass inventory development for the natural plant communities should include ground validation. Preference should be given to experimental determination of biomass constants rather than extrapolation from the literature.

GIS Databases. GIS maps or databases should contain a clear history of development, including criteria for classification and method of classification. The procedure for selecting training sites should be noted. GIS databases with a component of field validation are preferred over those generated from remote sensing data alone. Quantitative error estimation is possible, and recommended.

Use of Remote Sensing Data. At the present time, remote sensing from satellite platforms offers the capability of determining land cover classes where spectral characteristics are well-defined and distinct. However, establishment of plant identity at the species level goes beyond the normal capabilities of even advanced instrumentation, although color infrared aerial photography remains a useful technology where fine resolution is required.

California airsheds pose problems for remote sensing because of the variety of plant communities and the breadth of transition zones. Therefore, remote sensing should be coupled with field validation or comparison to maps or GIS databases where field validation has occurred. If the existing maps or database are found to be reasonably accurate, remote sensing could be used to identify and quantify future changes.

2.0 INTRODUCTION AND PROJECT GOALS

2.1 Background

It is well recognized (Finlayson-Pitts and Pitts, 1986; Seinfeld, 1986; NRC, 1991) that ozone and other gaseous and particulate secondary pollutants, are formed through the photochemical reactions of reactive organic gases (ROG), of both anthropogenic and biogenic origin, with oxides of nitrogen (NO_x). Extensive and effective emission control strategies by the California Air Resources Board (ARB) and the South Coast Air Quality Management District (SCAQMD) have led to a remarkable reduction over the past fifteen years in peak ozone levels, as well as in the numbers of first and second stage episodes, in California's South Coast Air Basin (SoCAB). Unfortunately, however, the SoCAB and several other major regions of the state (e.g. the Central Valley) continue to experience serious air quality problems (SCAQMP 1994).

An important study by the National Research Council (NRC, 1991) addressing the difficulties in further reducing photochemical smog, identified two major limitations in past attempts to model the contribution of ROG to the ozone-forming potential of urban atmospheres. One major finding was that the total inventory of ROG being emitted into the atmosphere from anthropogenic sources had been underestimated. Mobile sources, primarily automobiles, are responsible for the majority of hydrocarbon emissions in most urban airsheds, and accumulating evidence suggests that VOC emissions, including unburned gasoline, from mobile sources in the SoCAB (and perhaps other California airsheds) have been underestimated in the past by at least a factor of two and perhaps more (Ingalls *et al.*, 1989; Pierson *et al.*, 1990; Lawson *et al.*, 1990; Fujita *et al.*, 1992; Harley *et al.*, 1992; St. Denis *et al.*, 1994).

A second finding of the NRC study was that both regional and national inventories of hydrocarbon emissions from vegetation are not well understood (NRC, 1991). Emissions of hydrocarbons by vegetation has been known for several decades, resulting in significant research to quantify the emission rates from different plant species (Table 2.1). Experimental and modeling studies on an area-wide basis have demonstrated that biogenic hydrocarbons can constitute a significant contribution to the overall ROG

Table 2-1. Previous studies, methods for measurement for biogenic hydrocarbon emission rates, and adjustment algorithm used to normalize emission rates (adapted and updated from Winer *et al.*, 1989)

Investigator	Predominant Technique	Predominant Plant Species
Zimmerman (1979b)	Enclosure	Southern Forest Variety
Tingey *et al.* (1980)	Laboratory Chamber	Live Oak, Slash Pine
Arnts *et al.* (1982)	Tracer Model	Loblolly Pine
Evans *et al.* (1982)	Total Enclosure	Crops, Shrubs, Herbs, and Trees
Cronn and Nutmagul (1982)	Enclosure	Tropical Shrubs and Trees
Winer *et al.* (1983)	Enclosure	Natural and Ornamental Species
Yokouchi and Ambe (1984)	Mass Balance Chamber	Red Pine
Isidorov *et al.* (1985)	Branch Enclosure	Oaks and Pines
Lamb *et al.* (1985)	Enclosure and Micrometeorological	Deciduous Forest, Douglas Fir
Lamb *et al.* (1986)	Tracer Flux and Branch Enclosure	Oregon White Oak
Winer *et al.* (1989, 1992)	Enclosure	Agricultural and Natural Species
Juuti *et al.* (1990)	Enclosure	Monterey Pine
Monson *et al.* (1991)	Balanced Cuvette	Oak and Quaking Aspen
Guenther *et al.* (1991)	Enclosure	Eucalyptus
Corchnoy *et al.* (1992)	Enclosure	Potential Shade Trees
Janson (1993)	Enclosure	Scots Pine, Norwegian Spruce
Arey *et al.* (1995)	Enclosure	Native Species
Konig *et al* (1995)	Enclosure	Agricultural and Natural Species
Pier (1995)	Enclosure	Red Oak

inventory in both urban and rural regions (Zimmerman 1979a,b; Winer *et al.*, 1983; Chameides *et al.*, 1988; Pierce *et al.*, 1990; Lamb *et al.*, 1993). The significance of this contribution from biogenic sources is enhanced by the greater atmospheric reactivity of biogenic hydrocarbons in comparison to anthropogenic sources of atmospheric hydrocarbons. It is estimated that on average biogenic hydrocarbons are 2-3 times more reactive than emissions from mobile sources, the greatest contributor of anthropogenic hydrocarbons in the SoCAB (Atkinson and Carter, 1984; Atkinson, 1989; Corchnoy and Atkinson, 1990; Atkinson *et al.*, 1990; Atkinson 1990; Carter, 1994).

Recent modeling studies by the ARB have indicated that development of specific emissions control strategies for reducing ambient ozone concentrations in some areas of California are dependent upon estimated fluxes of biogenic hydrocarbons. These studies, using the Urban Airshed Model (UAM) with Carbon Bond IV chemistry, showed that emissions of hydrocarbons from vegetation can make the difference between NO_x emission controls or ROG emission controls being the most effective in reducing ozone concentrations (Jackson, 1994). Specifically, in certain airsheds, using the lower range of vegetative emissions estimates suggests ROG emission control strategies to be most desirable, while using the upper range of vegetative emissions estimates suggests NO_x emission control strategies would be most beneficial. Not surprisingly, modeling studies performed for other areas of California showed that vegetative hydrocarbon emission estimates become increasingly important as anthropogenic hydrocarbon levels are reduced in response to implemented and proposed control strategies.

However, the analyses of model simulation results in some cases have also suggested that emission inventories for biogenic hydrocarbons may be too high, or that there are other problems in the methodology being employed to evaluate the relative importance of vegetative emissions (Jackson, 1994). For example, a UAM simulation for the San Joaquin Valley resulted in predictions of ambient isoprene concentrations in excess of 750 ppbC whereas limited measurements of isoprene in ambient air in other airsheds suggested peak levels a factor of ten lower (Greenberg *et al.*, 1994; Biesenthal *et al.*, 1994). Also, two independently prepared vegetative emission inventories for the Sacramento area differed in both the quantity and spatial distribution of biogenic

hydrocarbon emissions (Jackson, 1994). These results suggested the possibility that biogenic emissions estimates prepared for California for use in photochemical modeling studies may be based on inappropriate estimates of any or all of the following: biomass and biomass distribution, emission factors, correction factors for diurnal and seasonal influences, and/or inaccurate coding within the available emissions models. As discussed below in Section 2.3, the objectives of the present project were developed to critically evaluate these and other key factors involved in assembling reliable biogenic emission inventories and models.

2.2 Previous Studies in California

2.2.1 South Coast Air Basin (SoCAB)

The first survey to determine the magnitude of hydrocarbon emissions from vegetation in a California airshed was completed with ARB support by Winer and co-workers in 1983 for the urbanized region of the SoCAB (Winer *et al.*, 1983). They employed a combination of aerial photography (Brown and Winer, 1986) and ground surveys with a stratified random sampling approach to determine vegetative biomass. Of the more than 180 species of vegetation identified in the study area (Miller and Winer, 1984), hydrocarbon emission rates were determined experimentally for approximately 60 of the dominant plant species. In addition, biomass constants (g per cubic meter) were developed for 51 plant species found in the Basin, permitting the conversion of crown volume to green leaf biomass (Miller and Winer, 1984).

Winer and co-workers used this estimate of biomass, along with the experimentally determined emission rates, to estimate the biogenic hydrocarbon emissions inventory for a portion of Southern California corresponding to roughly one-third the area of the SoCAB (specifically, the western and middle portion of the Basin containing most of the anthropogenic emissions of ROG and NO_x at that time). An upper limit estimate of vegetative hydrocarbon emissions for this study area was approximately 90 tons per day (TPD) during the summer, with a likely range of total isoprene and monoterpene emissions of 20 to 80 TPD (Winer *et al.*, 1983).

A more recent investigation by Horie and co-workers (Horie *et al.*, 1990) supported by the SCAQMD was designed to provide a gridded inventory of plant biomass in order to develop an improved hydrocarbon emissions inventory for use in the UAM. High- and low-altitude photography, in combination with ground surveys was used to identify vegetation in the SoCAB. More than 470 plant species were identified with a total biomass of approximately 8 million metric tons. Horie *et al.* (1990) also compiled an emissions rate database from the literature and suggested values for isoprene and monoterpene emission rates for the plant species identified in the biomass survey. For those species without measured emission rates, values were assigned based on the average emission rate for the structural class (conifers, broadleaf deciduous, broadleaf evergreen shrubs, etc.) of the plant. Correction factors were also applied to account for the effects of seasonal and diurnal changes in light and temperature on vegetative emissions and changes in biomass associated with seasonal changes (e.g. deciduous tree leaf fall).

The resulting data were used by the SCAQMD to develop spatially-resolved biogenic emissions estimates for each day of three ozone meteorological episodes (SCAQMP, 1991). These emissions ranged between 150 and 250 TPD, with the majority produced in the heavily vegetated mountain area downwind of the SoCAB.

Using the same biomass and emissions data compiled by Horie *et al.* (1990), Systems Application International (SAI) developed a temporally-resolved gridded inventory of vegetative hydrocarbons for the SoCAB (Causley and Wilson, 1991). The computer program "VEGIES" provided an hourly estimate of vegetative hydrocarbon emissions for each grid square (5 km by 5 km) in the SoCAB during an entire year utilizing temperature and light intensity correction factors and a canopy adjustment factor (EPA 1990) to model the effects of decreased light levels within the leaf canopy of trees. The results from the SAI survey indicated there were approximately 100 TPD of hydrocarbons emitted from vegetation during the summer compared to approximately 30 TPD emitted in the winter (Causley and Wilson, 1991).

In another recent study, sponsored by the California Institute for Energy Efficiency, Winer and co-workers have extended and refined the previous studies for the SoCAB by addressing four areas of uncertainty (Winer *et al.*, 1994; Benjamin *et al.*,

1995a,b). First, land-use distribution for the SoCAB was digitized on a Geographical Information System (GIS) at a 50 m resolution for urban portions of Los Angeles and Orange Counties, as compared to the 5000 m resolution of previous studies (Horie *et al.*, 1990; Causley and Wilson, 1991). Second, the existing database of emissions measurements was enhanced by the use of additional experimental measurements for emissions rates reported in the literature. Third, for more than 200 species without measured emission rates, emissions values were assigned based on taxonomic relationships rather than on the structural class of the vegetation (Benjamin *et al.* 1995b). Finally, a more realistic correction algorithm for environmental factors developed by Guenther (1991) was used in place of the Tingey *et al.* (1979) algorithm.

This study found total green leaf biomass for the SoCAB of approximately six million metric tons both in the winter and summer (neglecting vegetation leaf loss for natural species) with biomass concentrated in the forested mountains on the northern and eastern boundaries of the Basin (Benjamin *et al.* 1995a). Isoprene and monoterpene total emissions were estimated to be 110 TPD in the summer and 30 TPD in the winter, in good agreement with the results from Causley and Wilson (1991).

2.2.2 Central Valley

In support of an ARB program to develop biogenics emission inventory for California's Central Valley, including the Sacramento Air Basin (SAB) and San Joaquin Valley Air Basin (SJVAB), Winer and co-workers (Winer *et al.*, 1989, 1992; Arey *et al.*, 1991a,b) measured the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley. Four dozen individual compounds were identified as emissions from the agricultural and natural plant species studied.

Data obtained in this study demonstrated again there can be large variations in emission rates from a single specimen of a given plant species, as well as from multiple specimens of a cultivar. Mean emission rates for total monoterpenes ranged from none detected in the case of beans, grapes, rice, and wheat, to as high as 12-30 ug per hour for

pistachio and tomato (normalized to dry leaf and total biomass, respectively). Agricultural species were found to be overwhelmingly monoterpene emitters and not isoprene emitters.

In a follow-up study supported by the ARB, Desert Research Institute (DRI) developed a biogenics emission inventory for the SJVAQS/AUSPEX region, based on a combination of satellite imagery used to identify vegetation classes and Radian's Emissions Model System (Tanner *et al.*, 1992). Of 39 identified vegetation classes, one was agricultural, two were urban, three consisted of sand, water, or snow-covered areas with negligible biogenic hydrocarbon emissions and the remaining 33 classes were natural vegetation communities with varying degrees of specificity in plant species distribution.

For each species known to be present in each natural community, community-specific biomass factors were assigned, as were either measured emission rate factors or an emission factor (EF) based on a surrogate species from the same genus or family. Although a large portion of the species leaf biomass in the AUSPEX area was accounted for by plant species with measured EF or surrogate EF from species from the same genus, there were major uncertainties in EF assignments for important species in the AUSPEX area due to limitations in the experimental database.

Agricultural emissions were spatially defined only on a county basis, using a species mix of 10 crops identified as significantly emitting by Winer *et al.* (1989, 1992). Agricultural acreage for 1990 was used along with biomass estimates provided by Sidawi and Horie (1992) based on summaries of literature data. Based on county-wide data, Tanner *et al.* (1992) obtained a preliminary estimate that about 15% of the total biogenic hydrocarbon emissions by mass in the AUSPEX region, approximately 480 MTPD of a total of 3360 MTPD, were produced by agricultural crops.

Causley *et al.* (1991) have reported a study to estimate biogenic emissions for the Sacramento modeling domain in which a software system was developed to produce gridded hourly estimates of biogenic emissions for this area. Utilizing California-specific emission factors for individual plant species in conjunction with acreage and biomass factors by plant species, they generated emission estimates for isoprene and several monoterpenes. Emissions were spatially allocated using USGS GIS data for various land-

use categories, and the effects of environmental factors accounted for using Tingey algorithms and canopy shading adjustment factors.

Three 24-hour gridded biogenic inventories were generated for an August 7-9, 1990 episode, with total emissions of approximately 200 TPD. Isoprene constituted 37% of the inventory, and alpha- and beta-pinene and myrcene accounted for 95% of the monoterpene emissions. As in other studies of this kind, the authors noted the need to determine the sensitivity of the generated inventory to areas of large uncertainty, including biomass spatial allocation and measurements, assignments of known plant emission factors to species with unknown factors, and adjustments for canopy effects (Causley *et al.*, 1991).

2.3 Overall and Specific Objectives of this Project

The overall objective of this project was to critically and comprehensively evaluate the processes and databases with which biogenic emission inventories have been prepared for photochemical modeling in California, including those prepared for the South Coast and San Joaquin Valley Air Basins.

The specific objectives were to:

- Critically review and update currently available vegetative emission inventory biomass databases developed for photochemical modeling studies in California.
- Review emission rate factors used for vegetative species in California and update to reflect California's specific conditions. This would include supplementary relevant assessments and information concerning the biochemistry and physiology of biogenic hydrocarbon production and emission, the spectrum of biogenic VOC's emitted by vegetation, emissions of oxides of nitrogen from soil, and a review of the development of algorithms used to estimate terpene emissions under different environmental conditions.
- Review the availability and application of satellite imagery and aircraft photography for the development of biomass estimates for input to emissions models.

- Review currently available vegetative emission inventory models used to develop hourly, gridded emission estimates, recommend the best methods and models to incorporate into an overall vegetative emission estimation system for California, and determine which factors need to be updated for an accurate representation of the range of growing conditions in California.

- Identify specific information, gaps in databases, and areas of methodologies which require further research or data acquisition.

- Recommend procedures for verifying biogenic emission estimates used in photochemical models.

The remainder of this report describes the methods employed and results obtained for each of these tasks.

3.0 CRITICAL REVIEW OF BIOMASS ESTIMATIONS FOR THE CALIFORNIA SOUTH COAST AIR BASIN AND THE SAN JOAQUIN VALLEY AIR BASIN

3.1 Introduction

Knowledge of biomass, both species distribution and quantification of green-leaf mass, is essential in assembling reliable biogenic emission inventories. Unfortunately, emissions of isoprene and monoterpenes appear to be species-specific rather than correlated to more general biophysical parameters. Therefore, plant species identification remains a cornerstone for generation of precise emissions inventories. As discussed in detail above, certain plants in natural, urban and agricultural settings have been shown to contribute hydrocarbon emissions and the methods used for estimation of plant biomass can differ depending on the setting, the procedures employed, and the availability and use of remote sensing and GIS technologies.

The term biomass as used in this report is interchangeable with leaf mass, because woody parts of plants, and stems and roots of herbaceous plants, apparently are not significant sources of hydrocarbon emissions. Leaf mass for the purpose of emissions calculations is oven-dry leaf mass unless otherwise stated. No attempt is made within this chapter to distinguish plants which are native from those exotic introductions which are presently naturalized, that is, able to thrive with no human attention. Rather, the term natural vegetation used in this chapter refers to both native and exotic plants in unirrigated areas.

For this project, the review of biomass estimation focused on four studies. Two, the studies of Winer *et al.* (1983) (results also reported in Brown and Winer, 1986; Miller and Winer, 1984) and Horie *et al.* (1990), were for the South Coast Air Basin. Two, the studies of Tanner *et al.* (1992) and Sidawi and Horie (1992), were for the San Joaquin Valley Air Basin. These four studies represent the current best available biomass estimations for their respective airsheds.

A fifth study, that of Engineering-Science (1990), summarized biomass for the each county within California principally for agricultural crops, although 12 broad categories of natural plant communities were also included. This fifth study did not

present biomass data for specific airsheds and did not address urban or natural vegetation in detail. Consequently, the study does not appear to fall within the mainstream of biomass estimation research. A brief summary of the Engineering-Science (1990) study is presented in section 3.7.9.

3.2 Background Considerations

The two primary components of a calculation of hydrocarbon emissions from plants are amount of leaf mass and emission rate per unit leaf mass. Plant species differ in amount of leaf mass, leaf mass per unit volume and emission rate per unit leaf mass. Therefore, biomass data for emissions calculations are species-specific, which represents perhaps the most important consideration in gathering or analyzing such data. However, species identity is in itself not sufficient for estimating biomass. Even mature specimens of a single specie may differ substantially in canopy volume and leaf mass. For example, biomass ranged in variability from $\pm$ 8.6% for *Phyllostachys reticulata*, a bamboo, to $\pm$ 42% for *Fagus crenata*, a beech (Box, 1980).

The most direct and accurate method of determining biomass is destructive sampling, accomplished by removing leaves within a known volume from an individual plant, followed by drying and weighing. The ratio of leaf mass per volume is known as the biomass constant. Biomass of plants in the field may then be calculated by measuring the volume of a plant, and deriving the mass from the ratio of leaf mass to volume. Conversions may also be derived for biomass based on surface coverage of a plant. An alternative method of estimating biomass is to use published equations based on other plant data, such as DBH (diameter at breast height), or litterfall.

For well-studied species such as crop plants or forest trees cut for lumber, phenology models may be available. Phenology refers to development of a plant over time as influenced by climate and weather (Wells, 1980). Light interception as determined by remote sensing may be used to adjust canopy values (Cheung, 1991). Other remote sensing technologies may also be used (see Chapter 5, this report). At least one researcher has compared methods to estimate biomass and developed algorithms for its adjustment in several plant communities (Mutters, 1994).

Obviously, the most accurate method of biomass estimation remains destructive sampling on a site-specific basis. Sources of error for large-scale field estimates can be grouped into two categories. The first source of error is an inaccurate constant used for translating surface area coverage or volume of plants into biomass. Despite careful determination of a biomass constant, error may arise from the natural variability of foliage density. It should also be noted that very few biomass constants have been experimentally determined to date. The second source of error is incorrect estimation of the areal coverage of plant species. This error may arise from incorrect identification of species composition, from inaccurate measure of species presence in a mixed stand, or from inaccurate measure of land surface. Land surface area gauged from aerial imagery in mountainous regions should be adjusted by the cosine of the angle of slope since without adjustment land area will be underestimated, and appear from a planar view as 0.998 of the true value for a 6% (3.4°) slope and as 0.866 of the true value for a 58% (30°) slope.

Error estimations for biomass calculations in California airsheds have apparently not been made. However, for forest species, some quantification was given by Wells (1980). The error was likely to be 5-15% in estimating biomass from a single stand from sampling of trees within that stand, and 10-20% for reference trees from a similar stand in another location. Overall error for both land area and sampling combined was approximately 15-30% for a major species in a region with a large amount of forested land.

The latter error range could be used as a basis for comparison. For naturally vegetated regions within California airsheds, the error of calculation of biomass for each species could be expected at the high end of the 15-30% range and likely greater than 30% because of the high degree of endemism of the flora. Endemism is an ecological term referring to flora (or fauna) present in one location but not in another location in close proximity. A high degree of endemism may imply high species diversity and/or complexity of microenvironments. Natural communities in California are characterized by a high degree of endemism (Lenz, 1956; Munz and Keck, 1968). For urban areas, the range of error may exceed the approximate 15-30% range because of the great diversity

of horticultural specimens. In an agricultural setting, it is probably possible to decrease the biomass error from both factors to the low end of the 15-30% range, or below, because of the flat topography and detailed reporting of crop acreages.

Because of the labor and expense associated with field mapping of natural plant communities, historic documents such as the vegetation surveys made in the 1930's are still being used. A recognized assumption in using such references was that the composition of the communities changed little in intervening years. However, data from a remote sensing study of forested land in northern Minnesota showed rapid change of ecological states (Hall *et al.*, 1991). The forest states were clearings, regeneration, deciduous, deciduous/conifer and conifer. In just 10 years, 1973-1983, over half the elements changed identity in both wilderness and nonwilderness areas, while the composition of the forest overall was unchanged.

3.3 Approach To This Review

Four studies were critically reviewed with the goals of obtaining current perspective on the state of knowledge, evaluating the methods utilized, assessing uncertainties and identifying areas where further research is necessary. Review was directed toward both internal structure and external harmony with other literature. Effort was made to identify assumptions within the studies. All four studies represent major additions to the fund of knowledge concerning biomass estimation in California. The findings of this present review will contribute both to characterization of the uncertainties in emission inventories assembled using these studies, and to suggestions for refined approaches to future biogenic inventory development.

3.4 Winer *et al.* 1983, South Coast Air Basin

The 1983 study of Winer and twelve collaborating researchers represents the seminal work in quantitative estimation of biogenic emissions in the Los Angeles basin. This study approached biomass estimation through a tiered process of characterization and subsampling, (i.e. a stratified random sampling approach). The leaf biomass per volume ratios, that is the biomass constants, for 51 plant species were measured. For 10 plants

in the natural community, leaf biomass per unit cover area were also experimentally determined. An important component of the study was ground-based verification of aerial images to ascertain the identity and volume of plants. The approach of Winer and co-workers (1983) has been modified in subsequent studies, but important facets of their methodology and data reappear in later studies (e.g. Konig *et al*, 1995).

3.4.1 Scope of the Study

Land area of the study was 4505 km^2 on the west (source) side of the Los Angeles basin, extending from the Pacific Ocean shore to approximately the Santa Ana Mountains east of the 57 freeway. The Santa Ana mountains roughly bisect the Los Angeles basin. On the north, the boundary was the 3600 ft contour of the Santa Monica and San Gabriel mountains, and on the south, the intersection of the Santa Ana mountains with the Pacific coast (Figure 3-1). As would be expected, the majority of the area was urbanized (58%), followed by land forms of steep topography covered with natural vegetation (33%), areas identified as non-vegetated (7%) and vanishing agricultural lands (2%).

3.4.2 Delineation of Area Subsets

Subsets were determined through a stratified random sampling approach (Figure 3-2). Land within the study area was first divided into four land use categories: urban, natural, non-vegetated, and agricultural. The division was made on the basis of high altitude U-2 color infrared (CIR) photography (Brown and Winer, 1986).

The urban vegetation class was divided into 20 polygons. Polygons were outlined on the basis of uniform greenness, which presumably indicated a greater homogeneity of vegetation within polygon boundaries as opposed to between polygons. That assumption was later questioned in Horie *et al.* (1990) where the first tier of sampling was defined on the basis of land use classification alone.

Subsequently, one rectangular area per polygon was chosen at random for more detailed analysis. Each rectangle was overflown by low altitude aircraft to provide detailed CIR photographs. The rectangles averaged 0.3 km^2. Within each rectangle,

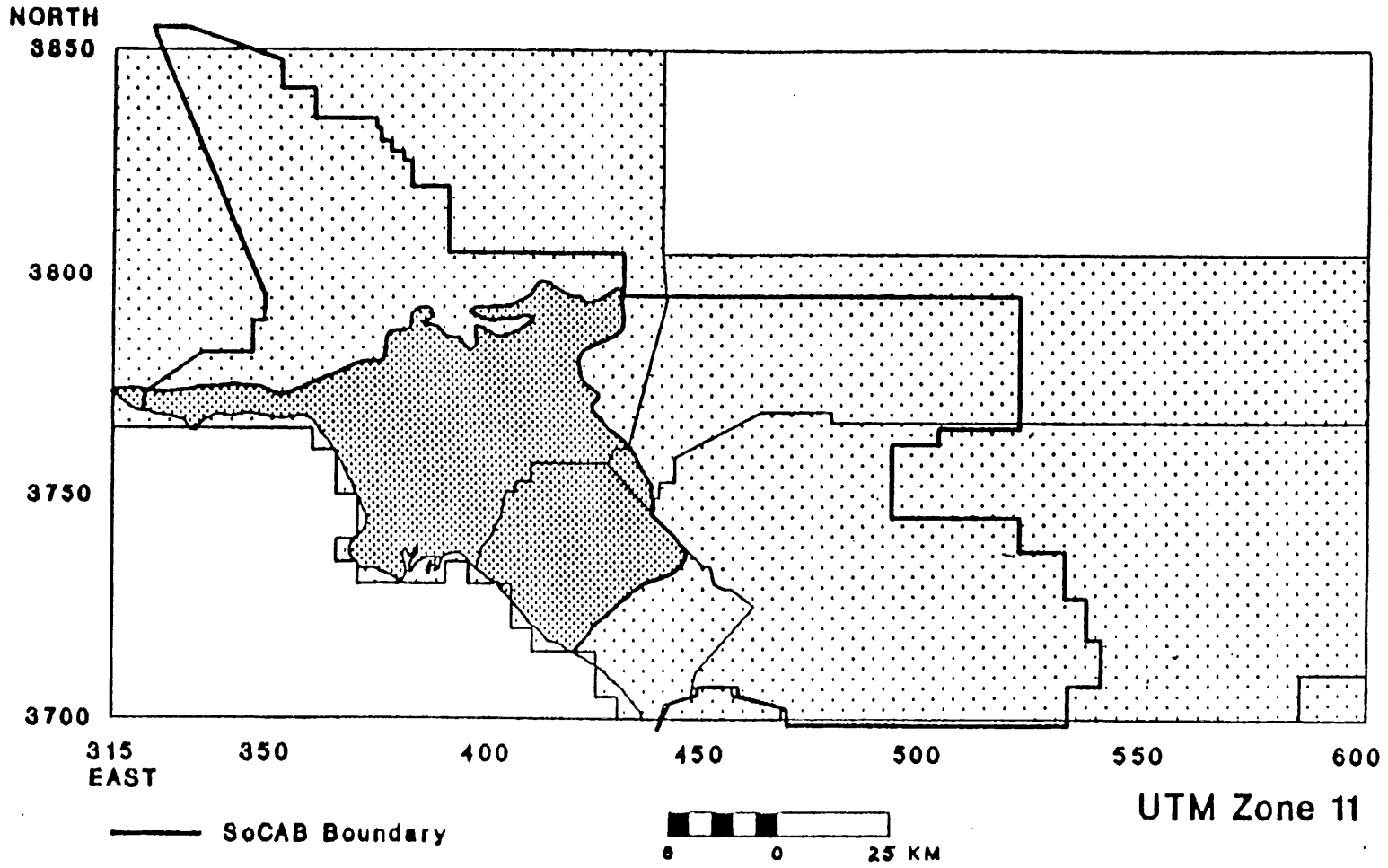

Figure 3-1. Geographical limits of the study regions of Winer *et al.* (1983) (dark shaded area), Horie *et al.* (1990) (shaded area) and the SoCAB boundary. From Horie *et al.* (1990).

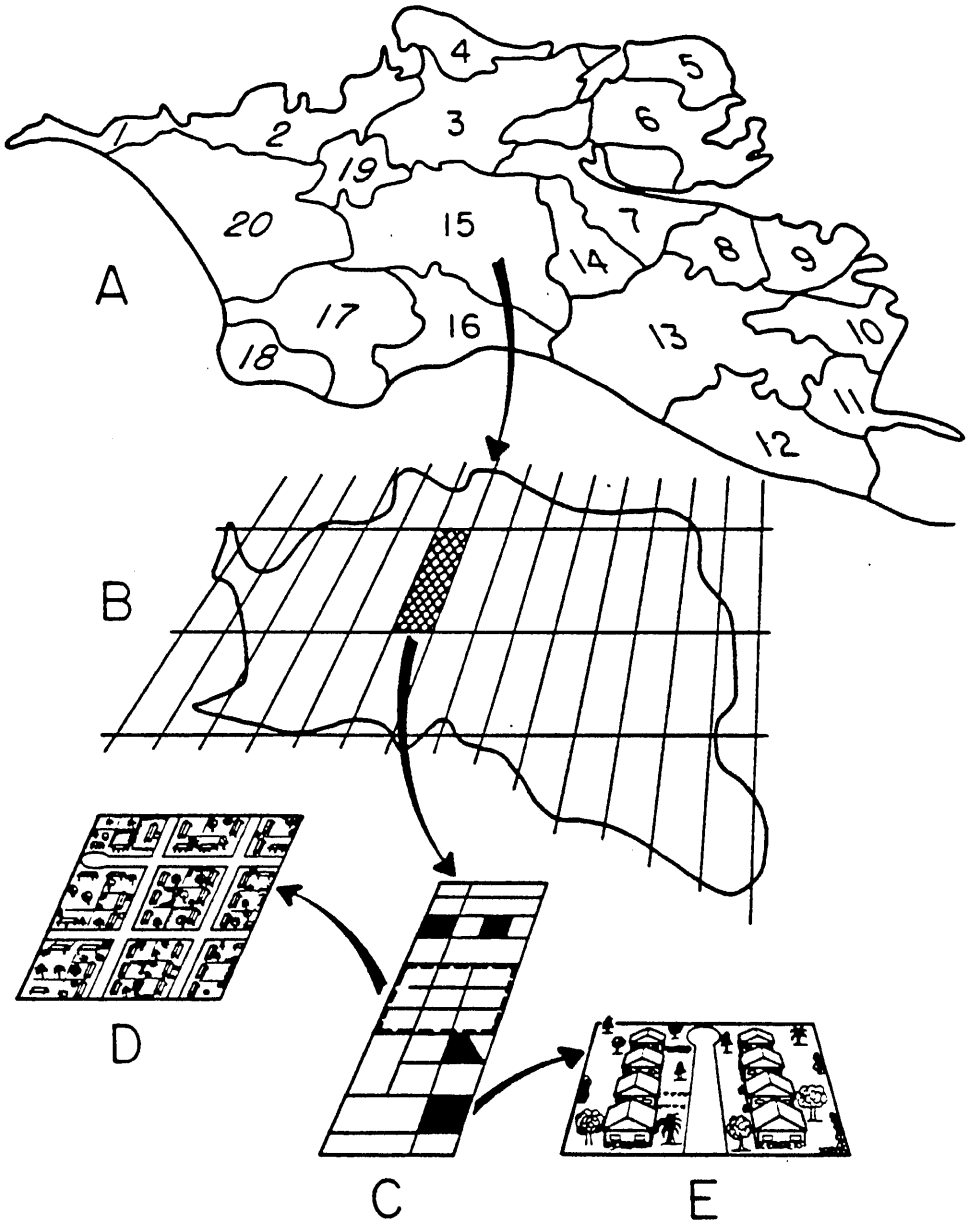

Figure 3-2. Depiction of the three-stage stratified, random sampling method used by Winer and co-workers (1983). A. Twenty stratified polygons covering urban portion of the study area. B. Polygon with sample cell grid and randomly selected cell. C. Randomly selected sample cell showing center frame of color infrared imagery (dashed line) and randomly selected subplots (darkened). D. Color infrared imagery area mapped for vegetation cover. E. Subplot randomly selected for vegetation inventory.

subplots of at least 1% of the area of the rectangle were chosen for plant identification and measurement by ground teams.

In the natural areas, vegetation type maps produced from field surveys during the 1930's were available. There were five such vegetation types in the natural areas: grassland, sagebrush, chamise chaparral, chaparral and woodland. It was thought that despite fire or other natural disturbances in intervening years, the vegetation would return to its previous state in a short period of time. This was a defining viewpoint held in concurrence by plant geographers and others considered to be authorities in that subject area. Field visits to plots in the natural areas were made by researchers in the 1983 study of Winer and coworkers, an important element of validation. The issue of accuracy of the type maps should be revisited and was found to be problematic by Mutters (1994) in his work in the Sierra Nevada. Also, vegetation was surprisingly variable over time in a wilderness area in a northern U.S. forest (Hall *et al.*, 1991).

A plant mix was assigned to the agricultural areas, and by definition no plants were in the non-vegetated areas. Actually, some plants may have been present in the non-vegetated areas, for example in old industrial areas. This possibility was addressed in the subsequent work of Horie *et al.* (1990).

Because of their small size, neither the agricultural nor the non-vegetated areas are discussed further in sections 3.4.3-3.4.6 of this report.

3.4.3 Plant Identification Within Subsets

As noted earlier, an important feature of this study was the combination of aerial imagery with ground validation to establish the identity of plants. In the urban area, plants found in sample rectangles within polygons were divided into five structural classes based on CIR low altitude aerial imagery. The structural classes were trees, palm trees, shrubs, groundcover, and turfgrass. Teams visited subplots within each rectangle to establish the identities of plants within each structural class, and that species distribution was assigned to the entire rectangle, and extrapolated to the entire polygon. A table of common and scientific names was provided for the 51 species for which leaf mass constants were determined. Eighty-eight plants occurring in at least one polygon were

identified by common name only, which gave rise to ambiguity in some identifications. For plants such as carob, there could be no mistake. However, maple could have included more than six species found in the Los Angeles basin, which have widely varying volume and leaf size.

In the natural areas, vegetation type maps were used to establish vegetation classifications. Also, teams visited a total of 106 plots scattered throughout the natural area to measure the species composition within each of the five vegetation types: grassland, sagebrush, chamise chaparral, chaparral and woodland. Because species composition may have changed from one geographical area to another, five geographical areas were identified. For example, the Santa Monica mountains may have held a different mix of plants compared to the Santa Ana mountains. Plot data from a vegetation class within a geographical area was applied to the entire vegetation class of the same area.

3.4.4 Area and Volume Calculations of Vegetation

In a procedure similar to that used for species identification, area and volume of plants were determined by a combination of aerial image analysis coupled with field visits. In the urban area, plant coverage in the rectangular subsample was measured by dividing plants into the five structural classes and measuring the area of each on the low altitude CIR photographs. Ground teams visited sites within the rectangular subsample and measured the volume and area of each plant within subplots.

In the natural areas, surface coverage of the five plant communities was taken from the vegetation type maps. Volumes of species were assigned based on geometric shapes and size ranges based on values given in Munz and Keck (1968).

3.4.5 Assignment of Leaf Mass Per Volume Constants

Leaf mass constants were experimentally determined for 51 plants. For shrubs, 10-20 samples were taken from different plants. For large trees, five samples were taken. Plants to be sampled were found at UCR or in natural stands. The volume of the plant was measured, then leaves were removed, dried and weighed. Calculation of leafmass per volume constants proceeded as a ratio of dry leafmass per volume. No leaf mass

constants were available for 88 kinds of plants found in one or more subplots, although their occurrence was less frequent than the 61 species for which biomass constants were determined (Miller and Winer, 1984).

3.4.6 Calculated Values

Calculated values appeared to represent a good estimation of biomass. The 88 kinds of plants for which no biomass constants were available were not included in calculations. Therefore, the total biomass was at least slightly underestimated.

3.4.7 Description of Uncertainties

Several uncertainties in the Winer *et al.* (1983) study were addressed in the 1990 report of Horie and co-workers, and these are discussed in section 3.5 of this report. The approach of Horie *et al.* (1990) of initial separation into land use classifications, which they call urban terrain zones, probably represented an improvement in internal homogeneity of vegetation compared to the polygons of the Winer *et al.* (1983) study. Inclusion of backyards and vegetation in old industrial areas probably represented an incremental improvement.

Although the overall validity of the vegetation type maps of the natural areas dating from the 1930's remained a source of potential error, field teams did sample plots in those areas (Winer *et al.*, 1983).

3.4.8 Summary of Winer *et al.*, 1983

This report represented the seminal study of biomass inventory development in the Los Angeles basin. Their stratified random sampling approach was followed in principle in later research. The coupling of aerial imagery and site visits for the urban area, and plant maps with field plot evaluation for the natural area, represented important methods of validation. The experimental values determined for biomass constants continue to be cited in later works.

3.5 Horie *et al.*, 1990, South Coast Air Basin

The 1990 study of Horie, Sidawi and Ellefsen had goals similar to the 1983 study of Winer and co-workers: compiling an inventory of leaf biomass and emission factors to develop an estimate of biogenic emissions in the SoCAB. The 1990 study was done "building on Winer *et al.*'s study" and as such represented an extension and revision rather than a completely new approach.

The 1990 study (Horie *et al.*) contained approaches with certain refinements in methodology based on four perceived weaknesses of the 1983 study of Winer and co-workers. The weaknesses were listed as the following:

- Lack of inclusion of the Antelope and Coachella valleys
- Lack of discussion of the distinctiveness of the vegetation density and types after the urban area was separated into 20 polygons
- Listing 11% of the urban area as non-vegetated even though, according to Horie and co-workers, substantial vegetation existed in those areas
- Lack of urban sampling in backyards, potentially leading to inaccurate determination of species and volumes of biomass

3.5.1 Scope of the Study

The study was directed toward estimation of biogenic emissions from both urban and natural areas in the SoCAB. A major change from Winer *et al.* (1983) was in expansion of the size of the study area (Figure 3-1). While Winer *et al.* (1983) focused on the western source area within the SoCAB, with a total study area of 4504 km^2, Horie *et al.* (1990) included virtually all of the SoCAB, and extended well beyond the boundaries of the SoCAB to the east and north. In this study, the area of the urbanized portion of the SoCAB was given as 4908 km^2 and the natural area of the SoCAB as 9052 km^2, for a total SoCAB area of 13,960 km^2. The total study area combining the SoCAB and outlying areas was 25,500 km^2. The effect of this change by Horie *et al.* (1990) was to include relatively larger areas of natural vegetation. The additional study area included the Coachella Valley and areas of middle-elevation desert in the Antelope Valley.

However, the majority of the additional area is either downwind during the normal daytime on-shore flow, and therefore is a receptor rather than a source area for typical ozone episodes in the SoCAB, or is outside the SoCAB.

3.5.2 Delineation of Area Subsets

Using high altitude aerial photography, area subsets were first separated by urban and natural designations and, once separated, further classification proceeded by different methods for urban versus natural areas.

The urban area was subdivided into 14 land use categories, called urban terrain zones (UTZ's). Ten different classes of various amounts and types of buildings were identified plus four non-built classes which were freeway, open areas, wooded land and natural area. Thomas Brothers photo atlases of Los Angeles and Orange counties were used as photographic references in conjunction with street maps. The UTZ's appeared to be recognizable, differentiable, and have the potential to contain different vegetation species composition and densities. They appeared to represent an improvement in homogeneity over the vegetation polygons of Winer *et al.* (1983).

The natural area was divided into vegetation communities based on vegetation type maps developed during the 1930's. No field validation was conducted. It was recognized that field surveys were probably above the level of resources allocated to this project. However, the contemporary accuracy of maps based on historic data remained an uncertainty.

3.5.3 Plant Identification within Subsets

Coverage of plants was estimated on the basis of aerial photographs taken by Ellefson in 1990 of the entire urban area. Plants were separated into six structural classes, and the area of each delimited. Urban areas were also surveyed by ground teams. Seventy sites distributed among 13 land use classes were surveyed, and plants identified. The report commented that the survey seemed to have achieved a stable estimate for the species composition of the four classes of trees, but not for shrubs or groundcovers. This is not surprising for shrubs, but, because of their volume per plant, further efforts at

identification would probably only have yielded incremental increases in accuracy. The term groundcovers includes a broad diversity of flowers and low herbaceous plants, and lack of a stable species estimate was similarly not surprising. Horie and co-workers made the salient observation that plant distribution in urban areas was not primarily based on environmental variables, but was strongly affected by cultural and economic factors.

Coverage of plants within the natural area was estimated via a sampling procedure. The natural area was divided into eight natural provinces, each of which had slightly different species compositions within cover types. A transparency with 25 regularly spaced points was placed on 5 km X 5 km grid cells of the vegetation type maps. Plant communities beneath each point were recorded. Proportion of total area within the grid occupied by each plant community was calculated based on incidence beneath all 25 points. Plant identity within each community was based on plot data taken as part of the vegetation type mapping surveys of the 1930's.

Vegetation of the few grid cells which were intermediate between urban and natural was categorized with a specialized procedure.

3.5.4 Area and Volume Calculations of Vegetation

For the urban area, coverage of plants was based on analysis of aerial photographs. Six structural classes of plants were identified from photographs: needleleaf evergreen trees, deciduous trees, broadleaf evergreen trees, palms, shrubs and groundcovers. Tree size was assigned to 1 of 4 size categories which were "drip-line" diameters of 1, 3, 5 or 10 m. For shrubs and groundcover surface area coverage was estimated. Volume of plants was based on conversion from field measurements made by the sampling team. Plants were assigned values within structural class by including a shape factor.

In the natural areas, surface coverage by species was made on the basis of plot data generated during the 1930's vegetation type mapping surveys. The data from Winer *et al.* (1983) were used, and additional data for the expanded study region generated. Volume assignments were made by multiplying coverage area by height as given in Munz and Keck (1968) with correction factors for plant shape and clumping of foliage.

3.5.5 Assignment of Leaf Mass Per Volume Constants

Biomass constants for both urban and natural areas were assigned based on literature values, almost exclusively those of Winer *et al.* (1983). For those plant species where no literature value was available, the biomass constant of a single plant species within the same genus, or family was used. Where no closely-related species had been measured, the mean of species within the respective structural class was used.

3.5.6 Calculated Values

Calculated values appeared to represent a good estimation of biomass. It was not possible to compare the biomass found by Horie *et al.* (1990) to that found by Winer *et al.* (1983). The report of Horie *et al.* (1990) summarized biomass by UTZ and gave an overall value per UTZ in kg/ha. The 1983 report of Winer and co-workers listed subplot determinations of biomass per structural class, but the total area of each subplot was not given, so that kg/ha could not be calculated.

3.5.7 Description of Uncertainties

This report represented a determination of biomass in the SoCAB which appears reasonably accurate. For the urban area, biomass appeared to be counted precisely, although the degree of variability within a UTZ was not quantified. Biomass constants were primarily taken from Winer *et al.* (1983), and there appeared no need to repeat that work. Species for which no biomass constant had been measured were assigned a constant of another species within the same genus, if available. Where no related species (i.e. within the same genus) had been measured, a constant was assigned based on the average for the structural class. Those values were 168 g/m^3 for broadleaf deciduous trees, 394 g/m^3 for broadleaf evergreen trees, and 646 g/m^3 for broadleaf shrubs. Prior to assigning constants, volumes of junipers and cypresses were adjusted because the insides of those plants are usually devoid of green vegetation.

For the natural area, biomass presented more of an uncertainty, because the spatial distribution was made wholly on the basis of maps based on decades-old surveys. This deficiency was recognized in the report, and identified as an area for future work.

Biomass constants for the natural areas were assigned in similar fashion to those for urban areas. Constants were assigned directly where plant species had been measured in the work of Winer *et al.* (1983). If no value had been determined by measurement, the value for a related species was assigned. Where no related species had been measured, a value of 435 g/m^3 was assigned, presumably representing a sort of grand mean for plants in natural communities.

3.5.8 Summary of Horie *et al.*, 1990

The study of Horie *et al.* appeared to be well-conceived and executed. The major uncertainty, and opportunity for improvement, rests within the natural plant community, specifically the validation or quantitative refinement of species coverage. An improvement of lesser potential importance could be made by experimentally determining biomass constants for more species. Finally, volumes of plants in the natural community could be determined in field plots and checked for corroboration with values calculated on the basis of Munz and Keck (1968).

3.6 Tanner *et al.*, 1992, San Joaquin Valley Air Basin

The San Joaquin Valley air basin is defined as the southern portion of the Great Central Valley of California, stretching from Sacramento in the north to the mountains south of Bakersfield as shown in Figure 3-3. The prevailing wind direction is northwest. The upper elevation of the airshed may be considered as 6000 feet in the eastern Sierras (Mutters, 1994). Limited marine air intrusions occur over the Temblor Mountains to the west.

The first, and perhaps only, estimation of biomass for use in calculating hydrocarbon emissions for the SJVAB was the ambitious study of Tanner and co-workers (1992). That study included urban, agricultural and natural areas of the SJV. The fundamental units of the study were vegetation classes. The 39 vegetation classes identified in the study referred to land areas of similar spectral characteristics in Landsat imagery. Classes included areas of agriculture, sand, water and snow, but most, 33 of 39, were natural vegetation communities.

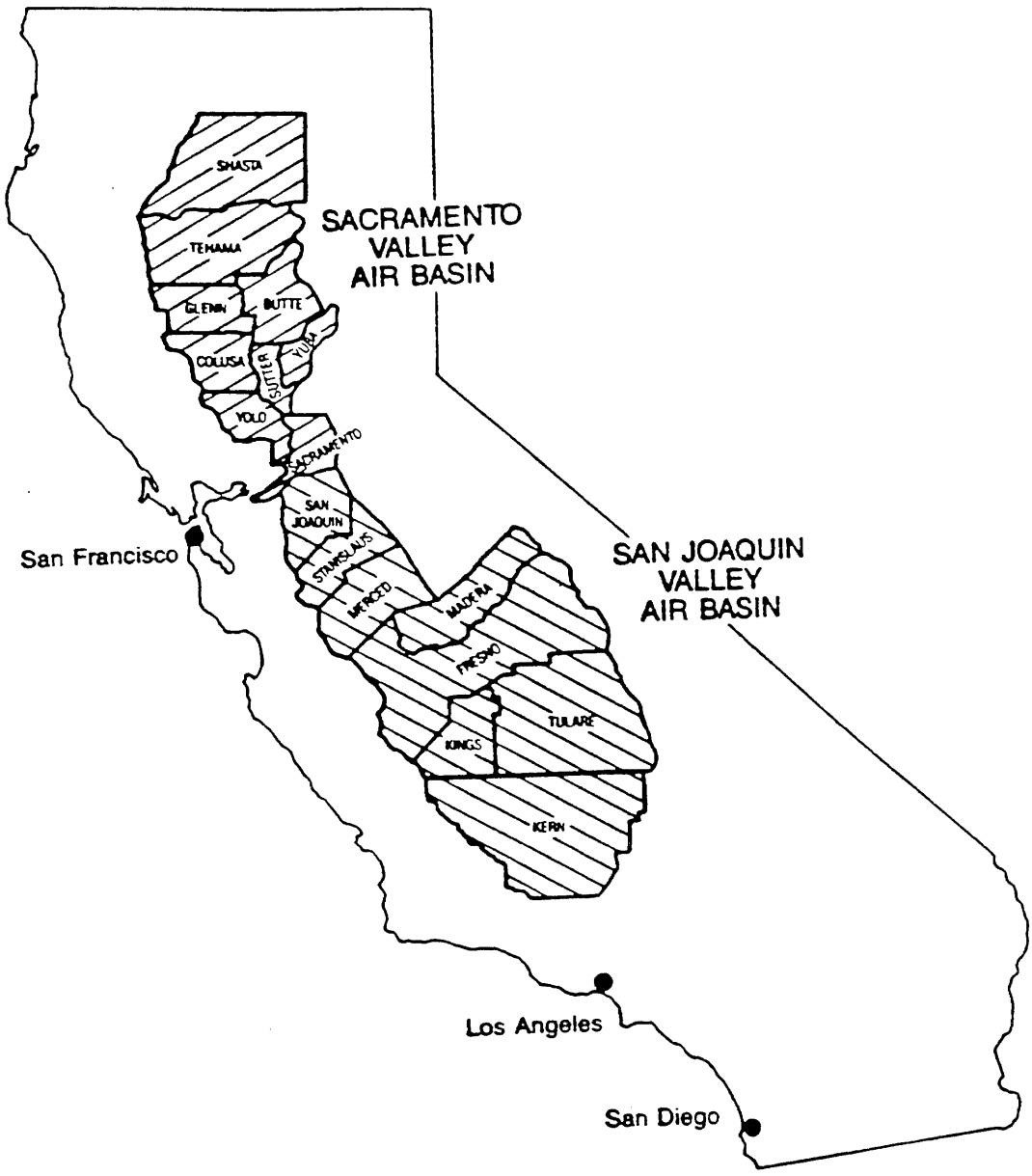

Figure 3-3. Map of California showing the San Joaquin and Sacramento Valley air basins which encompass California's Central Valley (Winer *et al.*, 1992).

3.6.1 Scope of the Study

The study region apparently also included the west side of the Temblor range, coastal urban areas, and extended north of the San Francisco Bay area. The additional area was outside the SJVAB but was included in an effort to combine the ARB San Joaquin Valley Air Quality Study with the related PG&E funded Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX) modeling effort (Figure 3-4). The biomass portion of the study developed an inventory within the SJVAB for natural, agricultural and urban vegetation. However, there are three important considerations related to the latter categories of vegetation.

First, agricultural emissions were estimated on a county-basis considering only "10 significantly emitting" agricultural crops (p.1). The source of emissions rate data was not cited. The crops identified were tomatoes, cotton, alfalfa, walnuts, almonds, pistachios, corn, wine grapes, raisin grapes and oranges. Raisin grapes presumably referred to table grapes. The table grape variety 'Thompson Seedless', by far the largest in acreage, may be dried for raisins or harvested for fresh market. The agricultural production of each county contained many more crops than these, and often of significant acreages.

Second, the method of estimation of agricultural acreages for the 10 crops appeared to be convoluted. In this study, DWR surveys of 1988 were used as the basis for estimating crop acreages. Changes in acreage from 1988-90 were then made, rather than using current census data from county Agricultural Commissioners, California Department of Food and Agriculture (CDFA). A census approach using data from CDFA was used to develop biomass estimates in the Engineering-Science report of 1990.

Third, land in urban areas was divided into three use categories but biomass data were not developed by Tanner *et al.* (1992). Rather, the data of Sidawi and Horie (1992), discussed in section 3.7, were used.

3.6.2 Delineation of Area Subsets

The fundamental units in this study were plant communities. Remote sensing provided the basis for the development of a GIS database. Landsat Thematic Mapper satellite imagery from 1983-85, utilizing six spectral bands, was used to develop a base

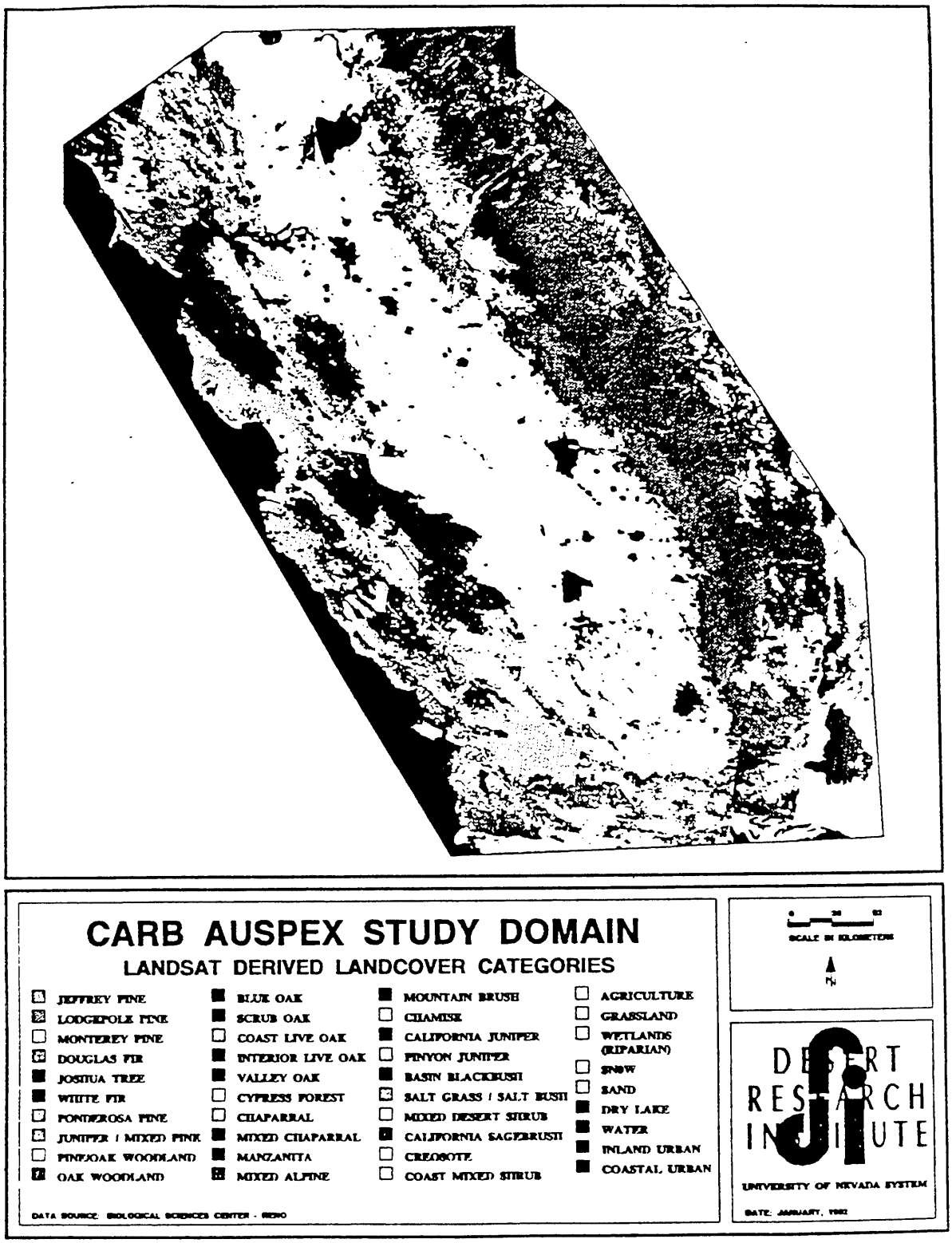

Figure 3-4. CARB AUSPEX study domain (Tanner *et al.*, 1992).

map for separation of plants into different communities. The normalized difference vegetation index (NDVI), a ratio of two bands, was added to the map to give a value for biomass density. (See Chapter 5 for further description and calculation of the NDVI.) The Landsat data were updated with 1990 high-altitude aerial photography. It was not clear whether or how much biomass values were adjusted based on NDVI or aerial photography. If NDVI was used, biomass for a whole community would be adjusted.

Plant communities were distinguished in the study area by coupling Landsat imagery to CALVEG via supervised classification. CALVEG, a GIS ARCINFO vector format database, is based on a series of hand-drawn maps developed during the 1980's (Keeler-Wolf, 1995) and was used as the primary historical reference for plant communities. CALVEG was compiled by the California Division of Forestry with a 1989 update for hardwoods by Allen *et al.* (1989). One of 99 possible plant communities is linked to each polygon in the entire CALVEG database.

Landsat images of the SJVAB were digitized and converted to an ARCINFO compatible format, followed by supervised classification. Supervised classification refers to assigning pixels to categories based on comparison to reference groups of pixels, known as training sets. (See Chapter 5 for further discussion of classification.) Three to 10 training sites were chosen from the Landsat imagery to represent spectral characteristics of each plant community. Training sites were identified based on CALVEG, aerial photography or staff knowledge. A numerical test was then performed to see if the remaining Landsat pixels could be separated based on the characteristics of the areas identified.

A fundamental assumption made was that CALVEG was accurate. According to Mutters (1994), 1993-94 field validation of CALVEG identification in southern Sierra experimental sites in the oak savanna, ponderosa pine and white fir revealed that community boundaries appeared to be correct. However, identity of the plant communities was not. The recent update by Allen (1991) has improved accuracy for the hardwoods region, but the veracity of CALVEG in coniferous forest and lower foothill elevations of the SJVAB remained untested. The minimum mapping unit in CALVEG was about 400 ha, corresponding to 988 acres, or about 1.5 square miles. That minimum

area represents a technical limitation of the database, making smaller communities or mixed patches difficult to represent.

3.6.3 Plant Identification within Subsets

Thirty-nine plant communities were identified in the study region after linking the Landsat-derived database to CALVEG. Of that number, one was agricultural, two urban and three sand, water or snow. Therefore, 33 communities of natural vegetation were identified. The authors stated " ... whose [natural vegetation communities'] spatial extent is highly resolved, but which vary in the degree of specificity of plant species distributions" (p.1). Within each community, qualitative plant species composition values were assigned from the literature.

3.6.4 Area and Volume Calculations of Vegetation

Area and volume calculations of plants within the natural community were contained within the community designations and were based on the literature. The calculations and area/volume relationships of plants within each community used to arrive at these figures were not presented in the report.

3.6.5 Assignment of Leaf Mass Per Volume Constants

For natural areas, biomass constants were apparently assigned based on literature values, and included within the plant community designations. Details of assignment of constants and calculations were not included in the report.

3.6.6 Calculated Values

Values of biomass were stated on a community basis. Total biomass for the region was apparently obtained by multiplying area of each community by its biomass value, although totals for the SJVAB were not presented.

3.6.7 Description of Uncertainties

The report of Tanner *et al.* (1992) provided an uncertainty estimation. Classification error was assigned a value of 0.15, meaning 85% accuracy for inclusion/exclusion of all vegetation classes. That value was based on previous work by the same authors and personal communication with remote sensing experts; accuracies of 85-90% have been reported for supervised classification of Landsat images. However, the Landsat image returned a single vegetation class value for all agricultural crops, i.e. different crops could not be distinguished. Urban areas were difficult to distinguish from the agricultural areas in the Landsat imagery. This appeared to reflect a limitation of Landsat imagery. If it was difficult to distinguish between agricultural and urban areas it would seem more difficult to distinguish among the gradual transitions of certain natural communities.

For biomass data, the authors assigned an error of 0.20 where species distribution in literature or survey biomass data were available, 0.50 where species distribution was known but total biomass was scaled to another community, and 0.90 where species were not known and biomass was scaled to another community. The authors state that " these are reasonable uncertainties for the average of all examples of specific vegetation communities, although individual polygons of vegetation communities may be more variable" (p.45).

3.6.8 Summary of Tanner *et al.*, 1992

The study offered a characterization of plant biomass in the natural communities, in the form of tables of species and biomass associated with Landsat-classified vegetation groups. A clear history of development of the classified Landsat image was presented, an important inclusion for work with a strong GIS component. The biomass data for urban areas is probably sufficient, especially considering the modest proportion of urbanized land in the SJVAB.

The estimation of agricultural crop acreages was arrived at circuitously. A direct estimation could have been made based on CDFA crop statistics. Beginning in 1990, reporting was required to County Agricultural Commissioners of all pesticide use on

crops, in addition to previous requirements for restricted use compounds. Consequently, current season records are kept for each field including acreage, crop type and location identified by section, township and range. Because virtually all crops, including organically grown commodities, receive at least one application of a chemical legally requiring reporting, the inventory of agricultural acreage in the SJV has been essentially complete. Data in 1995 were contained in Dataflex files, available from County Agricultural Commissioner offices, and transportable to a variety of computer systems. The data could be dumped into common delimited files and be read by most relational databases. In 1995, efforts were underway to identify field location in a gridded system (Brackeen, 1995).

In the natural areas, the main uncertainties arose from the length of the chain between remote sensing and assignment of biomass values without field validation. Of concern is the congruence of plant communities identified through mapping with those identified in the literature. There are a number of schemes of classification of plant communities, such as those of Allen *et al.* (1989), Holland (1986), and Munz and Keck (1968) which differ qualitatively in species composition. It was not apparent whether communities identified in the Tanner *et al.* study differed among themselves in levels of uncertainty in classification or in composition.

3.7 Sidawi and Horie, 1992, San Joaquin Valley Air Basin

The 1992 study of Sidawi and Horie was contemporaneous with that of Tanner *et al.* (1992) and covered the same land area, but the sole object was estimation of biomass densities. No summation of biomass in the SJVAB was given nor was emission rate information included. Biomass in urban, agricultural and natural areas was estimated using literature searches and some field validation. The study of Sidawi and Horie addressed a weakness of the Tanner *et al.* (1992) study, that of estimation of agricultural biomass density. As a result, the precision and accuracy appeared to be improved for these data.

3.7.1 Scope of the Study

The 1992 study of Sidawi and Horie covered exactly the same land area as that of Tanner *et al.* (1992). In the report, the SJVAB apparently also included the west side of the Temblor range, coastal urban areas, and extended north of the San Francisco Bay area. Although the study area is outlined as a rectangle (Figure 3-5), several field survey sites were outside the rectangle on the west side of the Temblor range and in the Bay area (Figure 3-6).

In natural areas, field sites were surveyed and data presented for those sites only. No estimate was made for biomass for the natural areas in entire SJV region. In agricultural areas, biomass densities for eight agricultural crops were estimated, but the crop acreages in the SJV were not. The estimation of urban vegetation biomass density was the most extensive part of this study. The method used was similar to that of the earlier study of Horie *et al.* (1990) for the SoCAB.

3.7.2 Delineation of Area Subsets

This study focused on the acquisition of biomass data for predetermined locations, based on mapping performed by Desert Research Institute and discussed in section 3.5 in the report of Tanner *et al.* (1992). Therefore, identification of land cover types was not a part of this study, except for urban land use classification. For urban areas, aerial photographs taken in 1989 were used to identify three land use types: urban residential, commercial/industrial and rural residential. Those three are likely to represent sufficient specificity. The approach taken in this study within the urban area, that of gathering species-specific data for different urban land use classifications, was justified by "the unique characteristics of urban vegetation, which is dominated by exotic trees and shrubs, with leaf biomass densities determined more by cultural practices than climatic, soil, and other natural conditions" (p. 2-2). Based on the plants listed, and irrigation practices in the area, that statement seems fully supported.

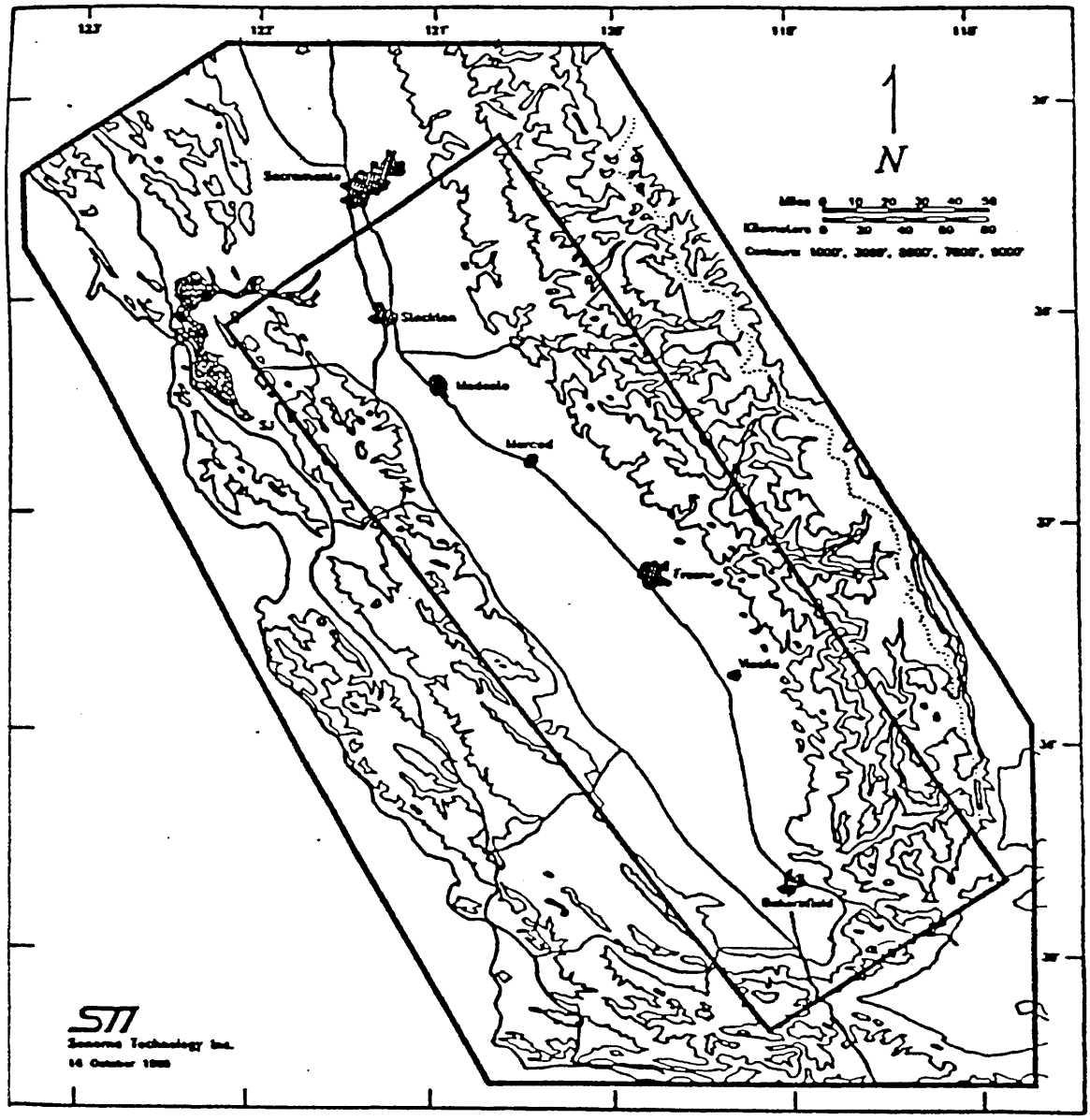

Figure 3-5. SJVAB-AUSPEX emissions inventory and modeling domain (Sidawi and Horie, 1992).

Figure 3-6. Field survey site locations (Sidawi and Horie, 1992).

3.7.3 Plant Identification within Subsets

3.7.3.1 Urban Subset

Fifteen field sites in Fresno were selected for ground survey. It was judged that those data could be applied to other urban areas in the SJVAB, such as Bakersfield, Modesto and Visalia. Plant lists developed during the Fresno survey are similar to those from the other sites. The climate is also very similar among those cities. Therefore, such an approach seems reasonable.

At each survey site, field botanists identified each plant found. Plants of some genera were not identified at the species level, such as eucalyptus, pines, roses and groundcovers. This is understandable for eucalyptus and roses because of the number of closely related species and extensive hybridization respectively. However, relatively few species of groundcovers and pines are found in landscaped areas of the SJV and it should be possible to identify them. A total of 20.85 ha were surveyed in urban areas, which would be expected to give sufficient indication of species present.

3.7.3.2 Agricultural Subset

Eight agricultural crops were chosen based on acreage or emission rate and where a more accurate determination of biomass density was judged necessary.

3.7.3.3 Natural Communities

Seventeen sites were subjectively chosen for field survey by DRI personnel in 1990 (Figure 3-6). The sites were chosen to reflect particular plant communities and to allow access. However, of the 17 sites, two were not actually surveyed due to difficulty in obtaining access from private landowners. Of the 15 sites actually surveyed, eight were located outside the SJVAB in the coastal or Bay Area counties of Santa Barbara, Monterey, San Mateo or Contra Costa. Of the seven sites within the central California, two were in mountain counties to the east of the SJVAB although the elevation may be low enough to have warranted inclusion in the SJVAB. Of the remaining five sites, four were located in Kern County and one in Madera County. No sites were surveyed in

Fresno or Tulare counties, which represent a large fraction of land area in the southern SJVAB and which contain extensive areas of natural communities.

3.7.4 Area and Volume Calculations of Vegetation

In the urban areas, plants were measured, and area for groundcovers or volume for trees and shrubs calculated. Crown volume of trees was estimated by taking the measure of crown height and diameter to calculate volume of a cylinder, then modifying by a shape factor and clump factor. For shrubs, a rectangular prismatic shape was assumed, and measurements made in three dimensions to calculate volume. Palms were measured on the basis of fronds, after the method of Winer *et al.* (1983).

For agricultural crops, data were gathered from the literature and researchers active in the field.

For the natural areas, a survey plot of about 2.5 ha was selected within each of the field sites chosen for study. Plants within the survey plot were measured for crown volume and cover.

3.7.5 Assignment of Leaf Mass per Volume Constants

No measurements were made of leafmass to volume ratios. Literature values of Winer *et al.* (1983) were used for individual species found in urban landscapes. Where a species had not been measured, a taxonomic approach was used, which assigned a value based on another species in the same genus. Where none of the species within a genus had been measured, a value was assigned based on the average of species within that structural class, e.g. broadleaf deciduous trees. Clearly, there is opportunity for refinement of this part of the inventory through actual measurements of leaf biomass per volume of unreported plants. However, for the SJVAB, the components of biomass represented by the agricultural and natural areas are much greater than the biomass found in the urban areas.

For the eight agricultural crops considered, leaf biomass constants were assigned based on literature values. Sidawi and Horie recognized that most biomass constants for agricultural crops were derived from plot data, and that plants grown in plots tend to have

more biomass than the same genotype grown in the field. Also, they recognized that no attempt had been made to incorporate the changes in biomass per volume which occur over a growing season. Several citations represent recent work, and that of researchers active in the San Joaquin Valley. Therefore, the values for biomass constants should represent an improvement over previous work.

For the natural areas, leaf mass constants were assigned based on the literature values of Winer *et al.* (1983). Where the species biomass constant was not reported, a constant of another plant within the same genus was used. Where unavailable, the average of the structural class (Horie *et al.*, 1990) was used.

3.7.6 Calculated Values

Values were presented without detailed supporting calculations. The values we checked by independent calculation were correct.

3.7.7 Description of Uncertainties

The urban areas comprised a small amount, less than 4%, of the total land area in the SJV. Therefore, uncertainties in leaf biomass or biomass constants for urban vegetation were less troublesome than for other types of land area.

For agricultural plants, Sidawi and Horie posited that leaf biomass values were reasonable to ± 20%, although no quantitative data were available. They listed several uncertainties. The most obvious was the change in vegetative biomass over the course of the growing season. Therefore, biomass constants reported represented the maximum. Other uncertainties in agricultural biomass constants were listed by them as the following:

- Leaf biomass data determined in other regions may not be applicable to the SJV because weather conditions have major effects on plant growth.
- Many crop types, especially vegetables, include dozens of varieties which may or may not have similar amounts of biomass.
- Biomass data are generally derived from plot experiments, which normally have higher amounts of plant growth than found under field conditions.

- Agricultural crops may vary in biomass within the SJV due to differences in environmental conditions.

Further refinement of biomass constants in agricultural crops is possible. For example, alfalfa biomass was considered to be the mean of plot data where compaction was a variable, and biomass varied by more than a factor of two depending on the amount of compaction. For cotton, only biomass from SJ-2 Acala cotton was reported. Pima cotton has since replaced Acala on a substantial acreage. Furthermore, since completion of the study, the 1993 arrival of the silverleaf whitefly has affected cotton cultural practices, and may have affected leaf biomass. Direct measurement of biomass/area relationships of crops grown in commercial fields offers a method of reducing these uncertainties.

For the natural communities, data for species distribution and volume were obtained from field measurements at 15 sites, but only 5 lay within the SJVAB proper. As recognized by Sidawi and Horie, the question remains of how uniform plant communities are, and therefore how applicable these data are to similar sites within the entire SJV region. They noted, "...both leaf biomass and species compositions in natural areas can vary considerably within cover types even between nearby sites. The large size of the study region suggests that geographical variation within cover types may be substantial" (p. 4-1).

3.7.8 Summary for Sidawi and Horie, 1992

The biomass values determined for the urban areas in the SJVAB represented the first data of their kind, and appear to be reliable. Biomass constants for agricultural crops were determined through literature review rather than experimentation, but appear to be an improvement over previous values. Site visits to the natural plant communities represent the first of their kind within the SJVAB, but their scope was limited. Much more could be done to characterize the natural plant communities within the SJVAB.

3.7.9 Engineering Science, 1990

A 1990 study, entitled Leaf Biomass Density and Land Use Data for Estimating Vegetative Emissions, was prepared for the U.S. EPA Region IX by Engineering-Science Design Research Planning of Berkeley, Ca. For natural plant communities, data from the U.S. Forest Service and the California Department of Forestry were used to list vegetation types and acreage in each California county. For agricultural crops, CDFA inventory data contained in corp reports were used. Literature values or extrapolations were used to arrive at a value of biomass per acre for vegetation types and agricultural crops. A summary of biomass per county of each crop or vegetation type was given. However, there were substantial uncertainties as noted in the following paragraphs. Also, the location of the plant communities or crops relative to specific airsheds were not given.

Vegetation in the natural communities was grouped into twelve categories, e.g. hardwood, mixed conifer, and montane chapparal. No quantitative definition of these communities was given. Because biomass was not known for all the plants in each community, biomass from known species was extrapolated to those with unknown leaf biomass. It was difficult to assess the accuracy of the biomass estimates because of these extrapolations. Also, it would be difficult to assign emission rates to vegetative types where the species composition is not known or not given.

For agricultural crops, leaf biomass was inferred from literature values. Leaf biomass could not be inferred for 22 crops, including tomatoes, peppers, and soybeans. The biomass values for 8 crops were reviewed and updated in the June 1992 study of Sidawi and Horie. Best estimates in that report differed as much as 130% from those in the Engineering-Science study. Values for some other crops reported by Engineering-Science were reviewed by Horie and Sidawi (1992), and judged to be adequate, although those crops were not listed.

3.8 Summary and Conclusions

The general approach taken in these studies was that of building a biomass inventory from the bottom up, consistent with the known requirements linking the flux of biogenic emissions to the amount of foliage per species. The stratified random sampling approach for inventory development in the urban areas appeared to be a reasonably sound and practical method of executing the estimation.

Quantitative estimates appeared reasonable for the SoCAB; however, because of differences in study area and data presentation it was difficult to quantitatively compare the work of Winer and co-workers (Winer *et al.*, 1983; Miller and Winer, 1984) to that of Horie *et al.* (1990). Also, because of the normal onshore flow, it is arguable whether plants in the far eastern portions of the SoCAB, especially in the Coachella Valley and high desert areas should be considered as "source" areas.

The inventory for the urban areas within the SJVAB appeared to be adequate.

Biomass within the SJVAB is found mostly in agricultural and natural settings. Refinement is needed for both. For agricultural areas within the SJVAB, a direct approach based on current-year CDFA data is recommended rather than the more circuitous route based on remote sensing. It is doubtful that remote sensing of agricultural areas can provide a better estimate in the near future than the actual inventories available of crops and acreage. Development within CDFA toward listing of crops on a geographical grid system further recommends this data source for possible compatibility with GIS databases.

For natural communities, further characterization of plant species distribution and/or community distribution and composition is needed. In particular, California state cooperative vegetation type maps and CALVEG should be validated, for example through selective ground survey. It is unlikely remote sensing alone can provide the level of detail necessary for an accurate biomass inventory. If the existing maps or database are found to be reasonably accurate, remote sensing could be used to identify and quantify future changes. It should be noted there is progress toward a standardized classification scheme for plant communities (Keeler-Wolf, 1995). The Ecological Society of America has a subcommittee to address vegetation standards and classification. A standardized

classification scheme for California is expected in print in late 1995, distributed by the California Native Plant Society.

Finally, where necessary, biomass constants could be determined in the field for agricultural crops and plants within the natural community.

4.0 CRITICAL REVIEW OF BIOGENIC EMISSION FACTOR DEVELOPMENT AND COMPILATION

4.1 Introduction

It is now well established that plants emit a wide variety of volatile non-methane organic compounds (NMOCs) including isoprene and various monoterpenes, sesquiterpenes, and oxygenated hydrocarbons (see, for example Sanadze and Tchiabriashvili, 1976; Graedel, 1979; Isidorov *et al.*, 1985; Winer *et al.*, 1989, 1992; Arey *et al.*, 1991a,b; Corchnoy *et al.*, 1992, Konig *et al.*, 1995). The influences these biogenic emissions have on ambient air quality has been of interest since they were first implicated as the cause of blue hazes which blanket forested regions, particularly in the summertime (Went, 1960). Subsequent studies have indicated biogenic NMOC emissions may exceed anthropogenic NMOC emissions on a global scale (Zimmerman *et al.*, 1978; Logan *et al.*, 1981) and are comparable to anthropogenic NMOC emissions for the contiguous United States (Lamb *et al.*, 1987, 1993).

Although the emission fluxes of biogenic NMOC's are expected to be significantly lower than anthropogenic NMOC fluxes in urban areas, the high photochemical reactivity of many of the biogenic NMOC's can increase their relative contribution to the formation of ozone and other secondary pollutants. In part because the high measured rate constants for the gas-phase reaction of biogenic NMOC's with the hydroxyl (OH) radical (Atkinson, 1989, 1994), biogenic NMOCs are estimated to have 2-3 times greater photochemical smog-forming potential than the organics in solvents or gasoline and the combustion products in vehicle exhaust (Carter, 1994). As a result, the significance of biogenic NMOC emissions cannot be ignored when attempting to design control strategies for compliance with ambient air quality standards. This conclusion is supported by modeling studies performed by Chameides *et al.* (1988) and other recent analyses (NAS 1991; Cardelino and Chameides, 1995; Geron *et al.*, 1995). For example, using average NMOC emission rates for vegetation in the Atlanta region, Chameides and co-workers determined that even if strict control strategies were employed to eliminate all NMOC's of anthropogenic origin, the biogenic emission inventory was sufficiently high in the presence of existing oxides of nitrogen to cause ozone levels to exceed the National Ambient Air Quality Standard of 0.12 ppm.

In order to model the effects of biogenic NMOC on the ambient air quality of a region, emission sub-models are employed. Examples include the Biogenic Emission Inventory System (BEIS) produced by the U.S. Environmental Protection Agency, the Vegetation Emission Inventory System (VEGIES) produced by the South Coast Air Quality Management District (SCAQMD), and Geocoded Emissions Modeling and Projections (GEMAP) system used in the San Joaquin Valley Air Quality Study (SJVAQS) Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX) Regional Modeling Adaptation Project (SARMAP). These models produce hourly gridded hydrocarbon emission data for use in larger ambient air quality models such as the Regional Oxidant Model (ROM) and the Urban Airshed Model. The input required for these models includes the vegetative composition and distribution in the area of study, the types and rates of NMOC emissions from the plant species contained in the area of study, and data for relevant environmental parameters (in particular, seasonal and diurnal temperature and light intensity variations).

The purpose of this chapter is to evaluate the current state of knowledge concerning the emission of biogenic NMOC's from plants, how those emission rates are measured, the chemical composition of such emissions, and the effect of environmental factors on emission rates. This chapter first provides a brief discussion of knowledge concerning the biochemical and physiological synthesis and release of biogenic NMOC's, the types of compounds emitted by vegetation, and their effects on ambient air quality. A discussion of various algorithms used to adjust emission rates for various environmental parameters (including temperature, light intensity, CO_2 concentration, relative humidity, and canopy effects) is also provided. Then a critical evaluation of biogenic emission rates and inventories developed for the California San Joaquin Valley and South Coast Air Basin is provided. Finally, an updated list is provided of normalized emission rates for all plant species which have been measured directly, and for important plant species for which emission rates which have not been previously measured for which estimates are available based on taxonomic relationships (Benjamin *et al.*, 1996b). A brief review of available information concerning NO_x (primarily NO) emissions from soil is also provided.

4.2 Composition of Biogenic NMOC Emissions

As mentioned above, investigations to characterize the composition of biogenic emissions have identified a wide variety of NMOC species, including isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons. Early studies tended to focus only on isoprene and selected monoterpene species (e.g. α-pinene, β-pinene, 3-carene, limonene and myrcene) but recent studies have illustrated the importance of oxygenated organics in the array of total emissions (see for example, Arey *et al.*, 1991a; Isidorov *et al.*, 1985; Lwanda and Bentley, 1987; Lwanda *et al.*, 1989; Tollsten and Bergström, 1988; Guenther *et al.*, 1991; Winer *et al.*, 1992; Konig *et al.*, 1995).

Tables 4-1 and 4-2 list approximately 80 different NMOC species which have been identified as being emitted from over 30 ornamental, agricultural and natural plant species found in the San Joaquin Valley in California and 17 arboreous plants characteristic of the forests of northern Europe, Asia, and North America, respectively (Winer *et al.*, 1992 and Isidorov *et al.*, 1985). Due to the limited number of plant species for which speciated emission studies have been performed, these lists are by no means expected to be comprehensive. Investigations by other researchers (Konig *et al.*, 1995) have identified NMOC species which are not contained on these lists, and it is likely that other plant species whose emission compositions have not yet been characterized contain additional compound types.

The particular distribution of organic compounds emitted from different vegetation types depends on the specific characteristics of each individual plant species and can vary widely. For example, in a study of NMOC emission rates from 28 indigenous species of vegetation in the Tampa/St. Petersburg region of Florida, Zimmerman (1979b) found the proportion of total emissions as isoprene and monoterpenes ranged from 0 to 100%, with 25% of the species emitting either no isoprene or no monoterpenes. For half of the plant species in this study, isoprene and monoterpene emissions accounted for less than 60% of the total emissions (Tingey *et al.*,1991). In a compilation of isoprene and monoterpene emission rates from vegetation found in the South Coast Air Basin of California, of the 123 plant species for which emission rates of these two NMOC types had been directly measured, 23% emitted only isoprene, 38% emitted only monoterpenes, 15% emitted both isoprene and monoterpenes, and 24% emitted neither (Benjamin *et al.*, 1996b).

Table 4-1. Compounds identified as emissions from agricultural and natural plant species (from Winer *et al.*, 1992)

Isoprene

MONOTERPENES
- Camphene
- 2-Carene
- Δ^3-Carene
- Limonene
- Myrcene
- cis-Ocimene
- trans-Ocimene
- α-Phellandrene
- β-Phellandrene
- α-Pinene
- β-Pinene
- Sabinene
- α-Terpenine
- γ-Terpenine
- Terpinoline
- Tricylene or α-thujene (tentative)[b]

SESQUITERPENES
- β-Caryophyllene
- Cyperene
- α-Humulene
- Other Isomers[c]

ALCOHOLS
- *p*-Cymen-8-ol (tentative)[b]
- cis-3-Hexen-1-ol
- Linalool

ACETATES
- Bornylacetate
- Butylacetate (tentative)[b]
- cis-3-Hexenylacetate

ALDEHYDES
- *n*-Hexanal
- trans-2-Hexanal

KETONES
- 2-Heptanone
- 2-Methyl-6-methylene-1,7-octadiene-3-one (tentative)[b]
- Pinocarvone (tentative)[b]
- Verbenone (tentative)[b]

ETHERS
- 1,8-Cineole
- *p*-Dimethoxybenzene (tentative)[b]
- Estragole (tentative)[b]
- *p*-methylanisole (tentative)[b]

ESTERS
- Methylsalicylate (tentative)[b]

n-ALKANES
- *n*-Hexane
- C_{10}-C_{17}

ALKENES
- 1-Decene
- 1-Dodecene
- 1-Hexadecene (tentative)[b]
- *p*-Mentha-1,3,8-triene (tentative)[b]
- 1-Pentadecene (tentative)[b]
- 1-Tetradecene

AROMATICS
- *p*-Cymene

[a]Unless labeled "tentative", identifications were made on the basis of matching full mass spectra and retention times with authentic standards.

[b]Tentative identifications were made on the basis of matching the mass spectra (and retention order when available) with published spectra (EPA/NIH Mass Spectral Data Base, and/or Adams, 1989).

[c]Several additional compounds were observed which can be assigned as C15H24 sesquiterpenes based upon their mass spectra and apparent molecular ions at *m/z* 204.

Table 4-2. Organics in volatile emissions of arboreous plants (from Isodorov *et al.*, 1985)

Compound	Plant Species	Compound	Plant Species
Propylene	8,9	Chloroform	16
Butylene	1-12, 15,16	Dimethyl sulphide	15
Isoprene	(1-4)**, 5-17	Santene	8,11
Hydrocarbon C_5H_{10}	1,2,5-9,13-15	Cyclofenchene	8-10,15
2-Methylbutane	1-8,12	Bornilene	8-17
2,3-Dimethyl butadiene	8,13,14	Tricyclene	7,8*,9,10
Hydrocarbon C_8H_{12}	8,9	α-Thujene	9,10,13-17
Hydrocarbon C_9H_{20}	1,6,11,16	α-pinene	3,(7,8,11,12,14)* (9,10,13,15,17)**,16
Methanol	15		
Ethanol	3-5,10,12-15	δ-Fenchene	9,10,12
3-Hexene-1-ol	1,2,5*,7,8	ε-Fenchene	9,12
Propanal	6	α-Fenchene	7-17
Isobutanal	16	β-Fenchene	7-10,12
Crotonal	17	Camphene	3,(7,9,10,12)*,(8,11)**, 13-17
Isobutenal	1-4,7,9		
Acetone	1-17	Sabinene	12,13,15,17,(14,16)
Butanone-2	8,13-15	β-Pinene	3,7-11,15
Methyl vinyl ketone	2,4	Myrcene	7-13,14*,15-17
Pentanone-2	6,8,15	3-Carene	7*,8-10,12-15,16*,17
Pentanone-3	5,7-10,15,16	α-Phellandrene	3,8-11
Furan	6	β-Phellandrene	8-11,14
2-Methyl furan	1-5,12,13	α-Terpinene	8-10,17
3-Methyl furan	1-5,12,13	β-Terpinene	3,8-10,13-15
Ethyl furan	1,2,4,8	γ-Terpinene	9,13-15,17
Vinyl furan	1,2,4,8	Limonene	3,7-17
Ethyl acetate	9	Terpinolene	9-17
3-Hexene-1-ol acetate	1,4-8	1,8-Cineole	3,8,14
Methyl (α-methyl) butyrate	14**	Fenchone	16*
		Thujone	16**
Methyl (α-methyl) capronolate	14	Camphor	8
		P-Cymene	7-17
Methyl chloride	14-16	Menthane	14

1) Bay-leaved willow
2) Aspen
3) Balsam poplar
4) European oak
5) European birch
6) Sorb;
7) European larch
8) European fir
9) Scots pine
10) Siberian pine
11) Silver fir
12) Common juniper
13) Zeravshan juniper
14) Pencil cedar
15) Evergreen cypress
16) Northern white cedar
17) Cinese arbor vitae

* Refers to those plants for the VOC of which this component is one of the main components
** Refers to the main VOC component

Whether a given plant emits predominantly isoprene and/or monoterpenes appears to be associated with plant phylogeny. It has been estimated that of an estimated 240,000 living plant species from some 400-600 plant families, only 144 individual species from 44 families are isoprene emitters (Bedell and Reveal, 1982), while the formation and emission of monoterpenes has been postulated to be confined to approximately 50 families of higher plants (Croteau, 1987). The dominant emissions from deciduous hardwood forests have been found to be isoprene (Flyckt *et al.*, 1980) while monoterpenes (in particular, α- and β-pinene) have been found to be the dominant emissions from coniferous forests (Winer *et al.*, 1989; Juuti *et al.*, 1990) (Very recently there has been a report from Europe (Staudt and Seufert, 1995) for the first time of light-dependent emission of monoterpenes by an oak species.).

While many different organic compounds have been observed to be emitted from vegetation, it has been reported that only a limited number of compounds generally dominate emissions on a mass basis. For example, in a study of trees in the forested regions near Baton Rouge, Louisiana, isoprene, α-pinene, β-pinene, d-limonene, myrcene, and sabinene constituted approximately 90% of the total emissions (Khalil and Rasmussen, 1992). Measurement of NMOC emissions from Monterey pine found that α-pinene and β-pinene accounted for over 80% of the total emissions (Juuti *et al.*, 1990). In a study of NMOC emissions from vegetation found in California's SJVAB, it was found that isoprene and a small number monoterpenes constituted 80-90% of total assigned plant emissions (Winer *et al.*, 1989). This generalization, however, does not always apply. Many individual plant species have been observed to emit significant quantities of NMOC's different from these compounds. For example, α-cedrene and (Z)-3-hexen-1-ol acetate were found to constitute 42% and 29%, respectively, of the emissions from *Vigna unguiculata* (Lwande *et al.*, 1989) and (Z)-3-hexen-1-ol acetate was also found to be the major emission (65%) from *Sorghum bicolor* (Lwande and Bentley, 1987). In addition, emission of various oxygenated organics have been shown to be comparable to, or greater than those of monoterpenes for a number of agricultural species in California's SJVAB (Winer *et al.*, 1992). Due to problems associated with sampling techniques used in early studies (e.g. steel cannisters) and the absence of GC-MS analysis, the importance of oxygenated organic emissions from plant species has been overlooked until more recent studies (Winer *et al.* 1992; Konig *et al.*, 1995).

Further research is required to evaluate the true importance of these emissions on ambient air quality for a given region.

Not withstanding the previous discussion, and while a great many organic compound classes have been observed to be emitted from vegetation, it appears that the bulk of the emissions are either isoprene or terpenoids (e.g. monoterpenes, and sesquiterpenes). Except for a small group of plant species, the emission of compounds other than isoprene and the terpenoids have been found to constitute only a minor portion of total NMOC emissions from many plant species. However, additional investigation is needed to more fully characterize the speciated composition of NMOC emissions from vegetation.

4.3 Biochemistry and Physiology of Biogenic NMOC Production and Emission

Understanding the mechanisms governing the synthesis and storage of biogenic NMOC's, such as isoprene, mono- and sesquiterpenes, and oxygenated compounds, is important since these mechanisms determine, in part, the accessibility of these compounds to the atmosphere. In spite of intense research into the mechanisms of synthesis and emission of these compounds, the factors controlling their emission rate have not yet been fully established. The purpose of this section is to provide a brief discussion of current knowledge concerning the synthesis and emission of biogenic NMOC's, how environmental parameters affect emission rates, and what future research is needed to develop a greater understanding of the processes governing these emissions.

4.3.1 Terpene Biosynthesis, Plant Physiology, and NMOC Emission

The biosynthetic pathway of the more common monoterpenes has been fairly well established and extensively reviewed (Croteau, 1987), and this process is shown schematically in Figure 4-1. The pathway begins with acetyl CoA and proceeds through the mevalonic acid pathway. Specifically, acetyl CoA is first converted to mevalonic acid pyrophosphate (MAPP) which is in turn converted to isopentyl pyrophosphate (IPP). IPP is then converted to dimethyl pyrophosphate (DMAPP). Subsequent condensation of a molecule of IPP and DMAPP results in the 10-carbon monoterpene precursor called geranyl pyrophosphate (GPP). Individual monoterpenes are then formed by the isomerization and cyclization of this 10-carbon precursor.

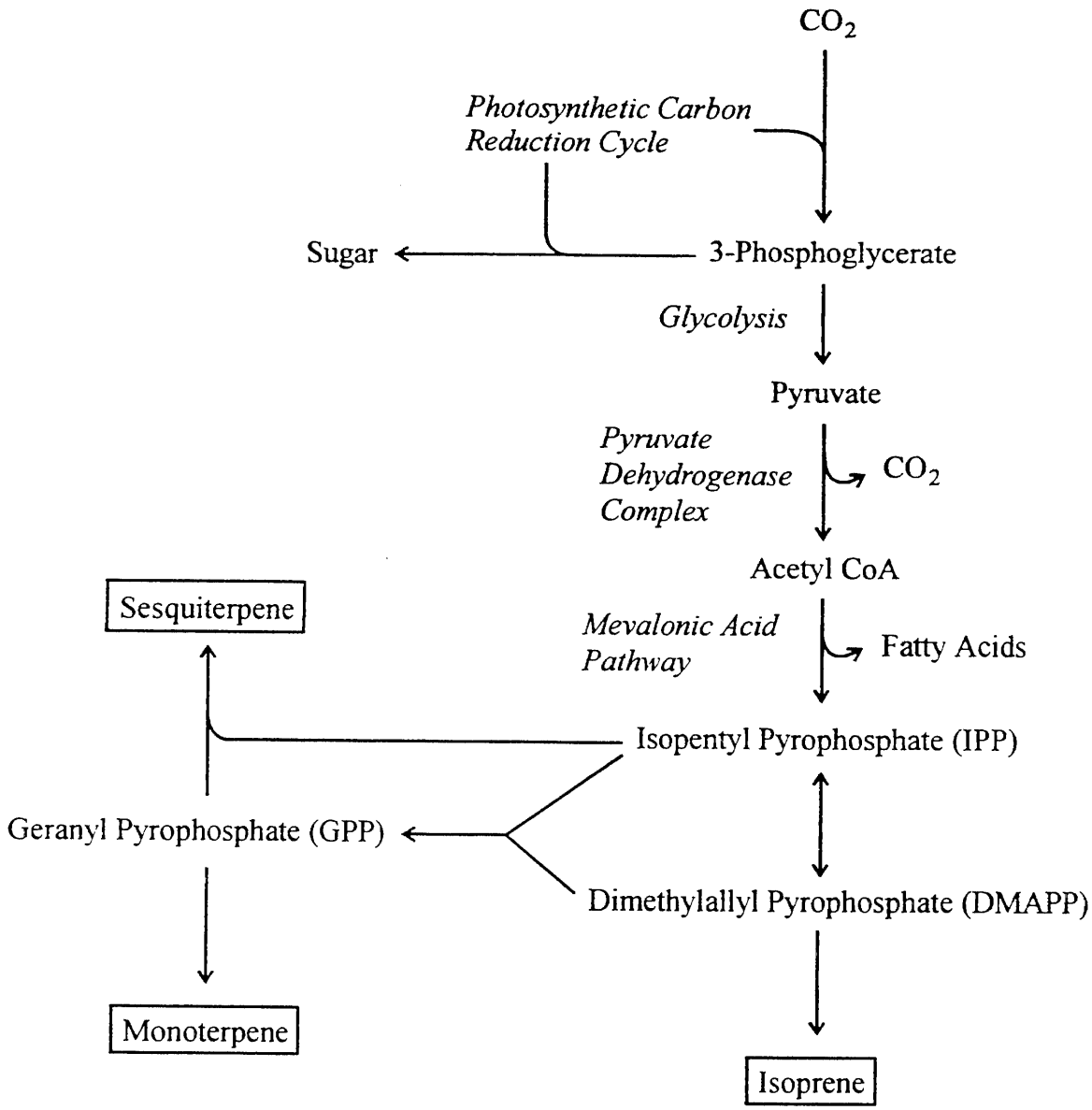

Figure 4-1. A simple pathway for the formation of isoprene and terpene precursors from CO_2 (adapted from Sharkey *et al.* 1991 and Dennis and Turpin 1990).

The 15-carbon precursor of a sesquiterpene is formed from the condensation of IPP and GPP. Subsequent isomerization and cyclization of this precursor structure leads to the formation of individual sesquiterpene molecules.

Sites of synthesis and storage of terpenes vary among different plant species which may result in different emission mechanisms. In herbaceous or shrubby families such as *Labiatae*, *Compositae*, and *Geraniaceae*, monoterpenes are stored in externally located glandular trichomes (Metcalfe and Chalk, 1950; Fahn, 1979) where emission is thought to occur through the cuticle (Tyson *et al.*, 1974; Fahn, 1979). On the other hand, many tree families such as *Myrtaceae*, *Rutaceae*, *Pinaceae* synthesize monoterpenes in specialized epithelial cells. Once synthesized, the monoterpenes are secreted into adjacent resin ducts.

The emission of monoterpenes in many plants with internal resin ducts is believed to occur through the stomata (Lerdau, 1991; Tingey *et al.*, 1991). However, monoterpene emissions have been observed to be independent of stomatal conductance (Thompson *et al.*, 1971; Monson and Fall, 1989). It has been suggested that constriction of the stomatal opening increases monoterpene and/or isoprene concentration within the leaf tissue. This higher concentration results in a larger concentration gradient, thereby increasing the diffusive driving force which compensates for the increased diffusive resistance that results from stomatal closure (Monson *et al.*, 1991a). Some monoterpene species, such as camphor from *Salvia mellifera*, are not emitted through stomatal openings, but rather directly through glands on the leaf surface (Dement *et al.*, 1975). These findings indicate the type of monoterpene emitted, the location of its synthesis and storage, and the leaf morphology and physiology all play influential roles in controlling monoterpene emission rates.

Tingey *et al.* (1991) developed a computational model to simulate α-pinene emissions from resin ducts. The model focuses on the diffusive processes governing the transport of α-pinene from the storage site through the mesophyl to the ambient air and takes into account many factors including: leaf temperature; vapor pressure of α-pinene; α-pinene water solubility; diffusion coefficient of α-pinene through leaf tissue; concentration gradient between the resin duct and the leaf surface; and leaf morphology and physiology. This model appeared to be consistent with available data for α-pinene and was able to account for a wide range of physiological and

environmental conditions. Further refinement and extension to other monoterpene species should provide valuable information concerning emission rate variability.

4.3.2 Monoterpene Emission Rate Variabilility Due to Environmental Conditions

By far, the most influential environmental parameter controlling monoterpene emission rate is temperature. Monoterpene emission rates have been shown to increase exponentially with temperature (see for example Tingey *et al.*, 1980, 1991; Yokouchi and Ambe, 1984; Juuti *et al.*, 1990; Guenther *et al.*, 1991, 1993). This increase in emissions with temperature has been attributed mainly due to increases in vapor pressure of the monoterpenes with higher temperatures. However, vapor pressure alone cannot account for all of the observed increase. For example, the vapor pressure of α-pinene increases 5.6% per degree of temperature change (Jordan, 1954) while emissions can increase by as much as 12.4% per degree (Tingey *et al.*, 1991).

This enhanced increase in α-pinene emissions is likely due to morphological and physiological changes in the leaf tissues which permits reduced resistance to diffusion from the storage sites to the open air. An alternate explanation for this reduced resistance is entrainment within the transpiration stream, with the water solubility of specific monoterpenes acting as the controlling factor (Tingey *et al.*, 1991). As leaf temperature increases, the amount of water passing through the mesophyll increases, resulting in an increased transpiration rate. As a result, monoterpene emissions will exhibit increased emissions due to either: (1) increased mass flow in the gas phase caused by the evaporation of water (co-volatilization), or (2) increased mass flow in the liquid phase due to increased flow of water and/or increased water solubility with higher temperatures. This explanation was suggested to account for different emission rates observed for different monoterpenes as a function of temperature (Tingey *et al.*, 1991).

Although light intensity has been shown to influence the size of the monoterpene pool by providing biosynthetic energy, controlling leaf physiology and photo-regulating monoterpene synthesis (Tingey *et al.*, 1991), it does not directly influence the short-term emission rate. Camphor emissions from *Salvia mellifera* in the dark were the same as in the light at a given temperature (Tyson *et al.*, 1974; Dement *et al.*, 1975). Monoterpene emissions from *Pinus*

elliottii, *Picea engelmannii*, and *Picea sitchensis* remained unchanged over a wide range of light intensities (Tingey *et al.*, 1980). However, over long periods of time, the depletion of monoterpene pools can affect emission rates. For example, *Salvia mellifera* plants held at 40 °C for 12 hours in the dark had lower emissions than plants held at 10 °C for the same time period under the same conditions (Dement *et al.*, 1975).

Nutrient conditions have also been implicated as causing significant influences on monoterpene pool size which may affect emission rates (Lerdau, 1991). These effects have been linked to long-term carbon metabolism. During periods of low water or nitrogen, plants have been observed to allocate more carbon to monoterpenes. Water deficiencies in *Pinus taeda* resulted in increased monoterpene pool levels (Hodges and Lorio, 1975). Nitrogen deficiencies resulted in increased levels of monoterpenes in *Heterotheca subaxillaris*, *Abies grandis*, and *Salix* species (Mihaliak and Lincoln, 1985; Muzika *et al.*, 1989; and Larsson *et al.*, 1986, respectively).

Monoterpene emission rates have also been shown to exhibit both qualitative and quantitative diurnal variation (Tingey *et al.*, 1991). Studies of cotton plants (*Gossypium Hirsutum*) found that total organic emissions were lowest in the morning and increased during the day to reach a maximum in the late afternoon (Thompson *et al.*, 1971). This emission pattern is likely controlled by diurnal temperature patterns. The composition of these emissions also changed through the day. Emissions of (E)-2-hexanol were substantial at mid-day but non-existent in the morning while sequiterpene emissions were greater in the morning than in the late afternoon. Similar diurnal variations were observed in studies of *Juniperus scopulorum* which found that sesquiterpene and oxygenated organic emissions increased throughout the day while emissions of sabinene decreased (Adams and Hagerman, 1977).

Seasonal variations in emission rates have been demonstrated in a number of plant species. Studies of Valencia orange trees showed emissions of linalool were a factor of ten higher during the blossoming season as compared to the average annual emissions outside this season (Arey *et al.*, 1991c). Emissions of α-pinene from *Pinus densiflora* were found to be lower in winter than would be expected based only on decreased temperatures as compared to summertime emissions. Similar seasonal variations were observed for other species including red oak (Flyckt, 1980), English oak (Dilts *et al.*, 1990) and forested regions (Isidorov *et al.*, 1985). Seasonal

allocation of carbon to monoterpene production has been attributed to phenological state where high monoterpenes production occurs during periods of high photosynthetic activity and limited growth rate (e.g. prior to bud break in the spring) but low production when both photosynthesis and growth rate are high (Lerdau, 1991).

4.3.3 Isoprene Biosynthesis and Emission

The biosynthesis of isoprene in green leaf tissues has been determined to be localized in chloroplasts (Mgaloblishvili *et al.*, 1978). Like monoterpenes, isoprene is believed to be enzymatically synthesized from IPP, which is formed from pyruvate and acetyl CoA through the mevalonic acid pathway (Monson *et al.*, 1991a; Loreto and Sharkey, 1990; Monson *et al.*, 1992; Dennis and Turpin, 1990; Sanadze, 1991). However, the sources of pyruvate and acetyl CoA in the chloroplasts remains undetermined. One possible source is 3-phosphoglyceraldehyde (3-PGA), which is derived from photosynthetic carbon (Sharkey *et al.*, 1991; Sanadze, 1991).

In contrast to monoterpene emission, isoprene emission is well correlated with photosynthesis. However, control of isoprene emissions is uncertain. Although the biochemical pathway of isoprene synthesis shares many of the same precursor molecules with monoterpene synthesis, since plants are unable to store significant quantities of isoprene (Sharkey *et al.*, 1991), the regulation of its synthesis and emission must be dependent upon its rate of photosynthetic mechanisms and/or the instantaneous availability of precursor molecules.

Numerous hypothesis have been presented to account for observed isoprene emission rates under a wide variety of conditions, however, complete elucidation of the control mechanisms has yet to be achieved. In a review on the biosynthesis of isoprene by Monson *et al.* (1991a), evidence is cited supporting a close linkage between isoprene biosynthesis and the photosynthetic electron transport chain. This evidence consists of the close dependence of isoprene emission rates on ATP and NADPH levels within leaf tissues. In contrast to this hypothesis, evidence is cited in a review by Sharkey *et al.* (1991) which supports the notion that isoprene biosynthesis is controlled by the pool sizes of carbon precursor molecules.

In a recent report, Sharkey and Loreto (1995) propose that the role of isoprene synthesis and emission is to provide thermal tolerance. Using nitrogen gas streams to suppress isoprene

formation, they observed irreversible leaf damage at 37.5 °C in a leaf without isoprene while damage occurred at 45 °C in a leaf given 17.5 ppm isoprene.

Although the evidence pertaining to each of these hypothesis is instructive, complete description of such evidence is beyond the scope of this project. Clearly, the regulation of isoprene biosynthesis is likely to be subject to complex control mechanisms which are at the present not well understood. Elucidation of these controls in the future will likely lead to better algorithms to predict isoprene emission rates under varying environmental conditions.

4.3.4 Isoprene Emission Rate Variabilility Due to Environmental Conditions

Although isoprene emissions have been found to be affected by light intensity, temperature, relative humidity, ambient CO_2 levels, water stress, and nutrient availability (see reviews by Sanadze, 1991; Sharkey *et al.*, 1991; and Monson *et al.*, 1991a), light intensity and temperature are believed to have the greatest effect on emission rates. Light intensity affects isoprene emission rates due to its close correlation with the photosynthetic process. As a result, isoprene emission is observed primarily during daylight hours, with nightime emissions being two orders of magnitude lower than daytime emissions (Sanadze, 1964; Tarkhnishvili *et al.*, 1985). Although Tingey *et al.* (1979) concluded that light intensity is a principal factor in isoprene emissions, leaf temperature was found to be the most important factor affecting actual leaf emissions. Temperature directly influences emission rate by changing the isoprene vapor pressure within the leaf and indirectly influences the emission rate by affecting the rate of enzymatic reactions associated with photosynthesis (Sharkey *et al.*, 1991). Over short periods of time, isoprene emission can increase as much as tenfold with a 10 °C increase in leaf temperature (Sharkey and Loreto, 1993).

As stated above, CO_2 and relative humidity levels have been found to affect isoprene emission. On a biochemical level, it has been shown that CO_2 concentrations which saturate the photosynthetic mechanism almost entirely inhibits the process of light-dependent isoprene synthesis (Sanadze, 1964; Tarkhnishvili *et al.*, 1985, Sanadze, 1991). As CO_2 levels were reduced to the compensation point, isoprene emissions gradually increased. As CO_2 levels were further reduced, isoprene emissions began to decrease until all CO_2 was removed and isoprene emission ceased. With regards to relative humidity, a 10% change in humidity was observed to

change isoprene emission rate by 1-3% (Guenther *et al.*, 1991). However, these effects were believed to be minor contributors to overall isoprene emission rates and have been deleted from recent environmental emission rate algorithms developed by Guenther and co-workers (Guenther *et al.*, 1991; Guenther *et al.*, 1993) as described in Section 4.8 of this chapter.

Little work has been published to date concerning seasonal variations in isoprene emission rate. Besides the obvious reduction in isoprene emissions due to seasonal biomass changes, isoprene emissions are likely to vary at different times of the year. For instance, seasonal effects have been reported for isoprene emissions from Red Oak (Flyckt *et al.*,1980). In addition, it has been shown that commencement of isoprene emission in Velvet bean and Eucalyptus leaves lags behind development of full photosynthetic capabilities in emerging leaves (Grinspoon *et al.*, 1991, Guenther *et al.*, 1991). Similarly, Monson *et al.* (1994) observed the springtime onset of isoprene emissions from Aspen leaves was delayed for up to 4 weeks following leaf emergence with maximal emission rates developing after 6 weeks. In contrast to studies showing a positive correlation between isoprene emission and leaf nitrogen content (Harley *et al.* 1994, Litvak *et al.* 1994), Monson and co-workers concluded that early season initiation of isoprene emissions was dependent upon factors other than leaf nitrogen concentrations. Further investigations concerning the seasonal variation in isoprene emissions in various plant species are needed to establish whether this effect has any profound influence on the total isoprene inventory of a given region.

4.3.5 Single Species Leaf-to-Leaf and Tree-to-Tree Variability in Emission Rate

At the present time, except for a very few cases, there are insufficient data to characterize emission rate variability between different leaves of the same plant and between different plants of the same species. Few studies have reported sufficient replicate measurements for this purpose. Even those few studies which do report replicate measured emission rates from individual plant species often do not supply sufficient information to calculate such variability with a high degree of confidence. For example, Winer *et al.* (1989) reported data from a study of agricultural species from California's Central Valley in which three separate emission rates from a single plant were measured at three different times of the day. However, it was not specified whether the measurements were taken from the same or different portions of the plant.

Therefore, it was not possible to calculate retroactively an estimate of leaf-to-leaf or branch to branch variability.

4.3.6 Summary of Emission Rate Variability

In summary, isoprene, monoterpene and oxygenated NMOC emissions exhibit wide variations both between and among different plant species due to biochemical and morphological differences, environmental conditions, and diurnal and seasonal variations. Knowledge of how these parameters affect emission rates is essential in making more accurate predictions concerning biogenic emission rates and therefore these factors deserve greater attention. At the present time, a number of these parameters are not considered when applying numerical computer models for estimating total NMOC emission inventories which may lead to inaccurate estimates of total emissions at different times of the day or year. Clearly, further research is needed to obtain a better understanding of the factors which regulate NMOC emissions in order to achieve more reliable estimates of their influence on regional and global air quality.

4.4 Atmospheric Transformations of NMOC Emissions

The ultimate role of different NMOC emissions from vegetation in affecting ambient air quality depends on their reactivity, atmospheric lifetimes, and the types of secondary products formed. When organic compounds are released into the troposphere, they undergo physical and chemical processes, including wet and dry deposition, photolysis, and gas-phase reactions with hydroxyl (OH) and nitrate (NO_3) radicals, and ozone (Atkinson, 1988, 1994; Bidleman, 1988). The atmospheric fate of a given organic compound will therefore depend on its particular chemical and physical properties. As a result, the reaction mechanisms and atmospheric lifetimes of these biogenic compounds must be understood in order to determine their potential impacts on air quality.

A comprehensive discussion of the state of understanding of the photooxidation mechanisms for isoprene, monoterpenes, and sesquiterpenes is beyond the scope of the present report and the reader is referred to the primary literature (see for example Shu and Atkinson, 1994, 1995; Aschmann and Atkinson, 1994; Atkinson 1994; Hakola *et al.*, 1994; and references therein). However, Table 4-3 lists calculated atmospheric lifetimes for various biogenic NMOC's

Table 4-3. Calculated atmospheric lifetimes of representative biogenic NMOC's (from Winer *et al.*, 1989).

Hydrocarbon	Lifetime with respect to reaction with		
	OH[a]	O_3[b]	NO_3[c]
Isoprene	1.8 hr	1.2 days	20 hr
Monoterpenes			
Camphene	3.5 hr	18 days	18 hr
2-Carene	2.4 hr	1.7 hr	35 min
Δ^3-Carene	2.1 hr	10 hr	1.1 hr
d-Limonene	1.1 hr	1.9 hr	53 min
Myrcene	52 min	49 min	1.1 hr
cis- and Trans-Ocimene	44 min	43 min	31 min
α-Phellandrene	35 min	13 min	8 min
α-Pinene	3.4 hr	4.6 hr	2.0 hr
β-Pinene	2.3 hr	1.1 days	4.9 hr
Sabinene	1.6 hr	4.5 hr	1.1 hr
α-Terpinene	31 min	3 min	4 min
Terpinolene	50 min	17 min	8 min
Aldehydes			
n-Hexenal	7.4 hr[d]	> 4.5 yrs[d]	190 days
Ketones			
2-Heptanone	1.8 days	> 4.5 yrs[d]	e
Ethers			
1,8-Cineole	1.4 days	> 110 days	e
Dimethoxybenzene	10 hr		3 yrs
p-Methylanisole	7 hrs		4 yrs
n-Alkanes			
n-Hexane	2.8 days	> 4.5 yrs[d]	13 yrs
n-C_{10}-C_{17}	7-31 hrs	> 4.5 yrs[d]	≥ 1.3 yrs
Alkenes			
C_{10}-C_{17} 1-alkenes	4 hrs[d]	1.3 days[d]	≈ 25 days

[a]For a 12-hr daytime average OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn *et al.*, 1987). Rate data used to calculate lifetimes taken from Atkinson (1989), Atkinson *et al.* (1990a), and Corchnoy and Atkinson (1989).

[b]For a 24-hr average O_3 concentration of 7×10^7 molecule cm^{-3} (Logan, 1985). Rate constant data from Atkinson and Carter (1984) and Atkinson *et al.*, 1990b).

[c]For a 24-hr average NO_3 concentration of 2.4×10^7 molecule cm^{-3} (Atkinson *et al.*, 1984 and Winer *et al.*, 1989). Rate constant data from Atkinson *et al.* (1990a, 1990b) and Corchnoy and Atkinson (1989)

[d]Estimated as discussed in Atkinson and Carter (1984) and Atkinson (1987).

[e]Expected to be of negligible significance as a tropospheric loss process.

with respect to reactions with the important tropospheric reactive intermediates (Winer *et al.*, 1989). Due to their short lifetimes (i.e. minutes to a few hours) most of these compounds are expected to react within a 24-hour period with daytime reaction occurring via the OH radical, nightime reaction via the NO_3 radical, and reaction with ozone occurring both night and day. As a result of these short atmospheric lifetimes, the specific compound emitted (e.g. specific monoterpene) may not be as important as the quantity of those emissions with respect to ambient air quality impacts within a given airshed.

The transformation products from the reaction of biogenic NMOC's with atmospheric oxidants undergo further transformations. For example, the products from the reaction of OH radicals with isoprene are methacrolein, methyl vinyl ketone and formaldehyde (Atkinson, 1990) and these products can react further (e.g. primarily via reaction with the OH radical or photolysis), or undergo removal by either wet or dry deposition. Although recent investigations have identified photooxidation products from the reaction of several monoterpenes and with the OH radical and ozone, further investigation is required to more fully characterize atmospheric transformation products from terpenes, including isoprene. (Atkinson, 1994; Hakola *et al.*, 1994).

4.5 Function of Biogenic NMOC Emissions

As discussed earlier, numerous studies by atmospheric and plant scientists have identified a spectrum of chemicals produced, stored, and emitted by plants. Atmospheric scientists have primarily focused on emission of these chemicals and their effects on tropospheric chemistry, while phytochemists and chemosystemasists have studied the metabolic synthesis and occurrence of these compounds in particular plant families. Although the function of these volatile organic hydrocarbons has been the subject of intensive research for the last 30 years, there still remains a fundamental lack of knowledge concerning the distribution of these compounds in plant tissues, their function, and the pathways of emission (Tingey, *et al.*, 1991).

4.5.1 Function of Monoterpene Emissions

The initial hypothesis concerning the production and emission of biogenic compounds suggested they were secondary metabolic products that accumulate within the plant during periods of water or nutrient stress (Mooney, 1972). If a plant does not have sufficient nitrogen and water

(which transports the nitrogen from the roots), solar energy can cause extensive damage to leaf tissues during periods of high light levels due to interruption of the photosynthetic mechanism (Field and Mooney, 1986). The disruption is speculated to be a result of an excess degree of electron flow due to light intensities above what is needed for photosynthesis (Tingey, 1991). However, the risk and amount of damage to the leaf can be attenuated if the plant is able to continue to utilize a portion of the incoming solar radiation by synthesizing compounds which don't require nitrogen such as isoprene, monoterpenes, and other NMOC's (Ross and Sombrero, 1991). In essence, the production of these compounds serves as a sink for the excess electrons which might otherwise cause damage to essential metabolic apparatus.

Most plants which experience only short periods of stress manufacture carbohydrates (starches and sugars). However, these compounds are attractive to herbivores and their long-term synthesis would be disadvantageous for survival. Therefore, many plants which exist in environments with extended periods of water or nutrient stress, as in Mediterranean climates, have developed the ability to produce other secondary compounds which not only protect the plant from photosynthetic damage but are also not attractive to herbivores. This adaptation can explain why Mediterranean ecosystems possess a large percentage of plants which contain so-called "essential oils" or secondary metabolites (Guenther, 1948-1952; Ross and Sombrero, 1991). While it has been reported that plants can utilize these materials in catabolic pathways (Coley *et al.*, 1985), their build-up in plant tissues would eventually become toxic unless the leaf is able to remove them. This could account for the substantial emissions of these secondary metabolites into the ambient atmosphere by certain plant species.

It has been postulated that plants have evolved other uses for these secondary metabolites. Their function as defensive compounds has long been known (Harborne, 1988). Many monoterpenes have been implicated as compounds which are effective against plant pathogens and fungi, and wounding of trees stimulates the production of these compounds (Walter *et al.*, 1989). Certain monoterpenes have also been postulated to serve as attractant pheromones both in their original form (Guerin *et al.*, 1983) and after autooxidation (Hunt *et al.*, 1989). In addition, monoterpenes have been identified as being allelopathic to other shrubs. The presence of bare zones between plants such as *Artemisia californica* have been attributed to phytotoxic effects of monoterpenes (Muller, 1970).

4.5.2 Function of Isoprene Emissions

At the present time, none of the functions ascribed to monoterpene emissions have been observed for isoprene. It is known that isoprene emissions make up between 0.5 and 2% of the carbon fixed through photosynthesis (Tingey *et al.*, 1979). This figure can reach as high as 8% is some tree species (Quaking Aspen, *Populus tremuloides*; Monson and Fall, 1989). Since isoprene is known to be neither stored nor used directly by the plant, the question remains; why would a plant continue to invest substantial efforts in the production of isoprene when it has such a high rate of loss. It is conceivable that isoprene is produced for one of the same reasons monoterpenes are produced, as a sink for excess electron flow under high light regimes. Since it is known that isoprene is directly coupled with photosynthetic processes (Sharkey *et al.*, 1991), this is a reasonable explanation.

An alternate explanation may be that isoprene, with its affinity for ozone and other oxidants, may protect the leaf from damage from these oxidants. The finding that ozone directly affects photosynthetic capability and dramatically reduces the carbon fixation rate provides support for this hypothesis (Weinstein and Beloin, 1990). The pathway for ozone introduction into the leaf is through the stomata (Reich, 1987), which is also the pathway for isoprene emissions from the leaf. If isoprene reacts with the oxidants prior to their reaching the internal photosynthetic structure of the leaf, then a 2% investment for isoprene synthesis would be advantageous for the plant.

Very recently, an additional explanation has been advanced as to why plants emit isoprene. Sharkey and Loreto (1995) have proposed that isoprene provides thermal protection to leaves by dissolving into membranes and altering their properties or membrane-protein interactions to increase thermal tolerance.

4.6 Experimental Methodologies for Determination of Biogenic Emission Factors

A number of different methodologies have been employed to measure emission rates of biogenic NMOC's. These methods fall into two general categories: chamber measurements and ambient atmosphere measurements (which includes tracer studies and micrometeorological gradient profiles). While each of these methods provides useful information concerning biogenic

NMOC emission rates, each also has drawbacks. This section provides a discussion of each of these methods, and identifies advantages and disadvantages unique to each of them.

4.6.1 Enclosure Methods

Enclosure, or chamber, measurements involve placing either a whole plant or a portion of the plant into an enclosure where NMOC emission rates are measured using dynamic flow-through techniques (see for example Zimmerman, 1979b; Tingey *et al.*, 1979; Winer *et al.*, 1983, 1989, 1992; and Arey *et al.*, 1991a,b,c). In the method of Zimmerman (1979b), a collapsible Teflon bag was placed over a portion of the plant, inflow and outflow gas tubes were placed along the stem of the branch and the bag was sealed. Once the enclosure set-up was completed, as much air as possible was removed from the bag and the bag was then re-inflated using "zero air" (approximately 80% nitrogen, 20% oxygen and 365 ppm carbon dioxide). Once the bag was re-inflated, the airflow was continued for 6 minutes at a rate of 10 liters per minute to allow a steady state concentration of NMOC to be achieved. Air samples were then taken by pumping samples into a stainless steel canister. These air samples were then analyzed using gas chromatography (GC). The identities of the NMOC emissions were determined using standards. Emissions from leaf litter and pasture samples was accomplished through a modification where the Teflon bag was attached to a stainless steel bag collar. This collar was then driven into the ground to obtain a seal. Emission measurements were then performed as described above.

The method employed by Winer *et al.* (1983) for plant species in Southern California was a modification of the Zimmerman procedures and corrected for a number of inherent problems. The primary deficiency of the procedures used by Zimmerman was that substantial plant disturbance could occur during the set-up and sampling processes. It was believed by Winer and co-workers that disturbing the plant could result in anomalously high measured emission rates, and this was later verified by the work of Juuti *et al.* (1990) who found that emissions from Monterey pine were increased by factors of 10 to 50 when the plant specimens were handled roughly. Additional discussions of "rough handling" effects on emissions have been reported as well (see for example Arey *et al.*, 1991, 1995; Winer *et al.*, 1983, 1989, 1992).

To minimize disturbance of sampled plant specimens, Winer *et al.* (1983) employed a rigid Teflon chamber. In this system, the Teflon bag was supported by a rigid frame constructed

of PVC pipe and the inlet and outlet ports were attached to the bag itself rather than running along the branch and included in the seal. Special efforts were made to minimize disturbance of the plants while enclosing the plant in the Teflon chamber. For measurement of NMOC emissions from groundcover species, instead of driving a metal collar into the soil around the sample material, samples were grown in plastic flats and placed on a pedestal to which the chamber could be tightly sealed. These two modifications in sampling technique were implemented to minimize plant disturbance prior to and during measurement.

A second deficiency of the earlier study by Zimmerman (1979b) was the lack of air mixing in the chamber. To correct for this, Winer *et al.* (1983) introduced a Teflon coated fan into the chamber to facilitate mixing. In addition, longer equilibration times (e.g. about ten minutes) were allowed prior to sampling to ensure steady state NMOC concentrations, since in preliminary studies, Winer *et al.* (1983) determined that exchange of approximately three chamber volumes of air was necessary to reach steady state consistent with the chamber acting as a stirred flow reactor. A fourth modification was humidification of the inflow air (along with the addition of CO_2) to better simulate ambient atmospheric conditions (humidification of flow-through air was not done in the Zimmerman (1979b) study). Finally, while Zimmerman (1979b) used stainless steel canisters for hydrocarbon sampling, Winer *et al.* (1983) utilized 10 ml silyated glass tubes. These samples were quickly analyzed (within 1 to 10 minutes). Based on preliminary evaluation of several sampling techniques, this sampling method was found to improve data reproducibility and reliability.

Although in a subsequent study of agricultural species in California's SJVAB, Winer *et al.* (1989, 1992) performed emission rate measurements using the same apparatus as in their previous study, their method of sampling was modified. In this study, air samples from the Teflon chamber were collected on Tenax and Carbosieve solid adsorbents, either singly or in combination, followed by thermal desorption for GC-FID or GC-MS analysis. The increased sample size (1-2 liters vs. 10 ml, respectively) afforded by this new collection technique was an improvement over the method employed by Winer *et al.* (1983). The basic enclosure, sampling, and analytical protocol developed by Winer and co-workers (1983, 1989, 1992) has been adopted in subsequent studies of this kind (see for example Arey *et al.*, 1995 and Konig *et al.*, 1995).

Other enclosure style techniques have been utilized in the measurement of NMOC emission rates by other researchers (see for example Tingey *et al.*, 1979; Evans *et al.*, 1982; Cronn and Nutmagul, 1982; Yokouchi and Ambe, 1984). Each of these measurement techniques were fundamentally similar to the methods described above. The only significant differences were in the specific design and construction of the chambers and in the specific protocols used to determine emission rates with GC and/or GC-MS analysis.

A fundamentally different enclosure-type methodology used to determine biogenic NMOC emission rates involved the use of leaf cuvettes (Monson and Fall, 1989; Monson *et al.*, 1991b, 1992; Guenther *et al.*, 1991). It consisted of clamping a single whole leaf (or a portion of a leaf) into a small leaf chamber or cuvette where emissions were sampled from a dynamic air flow system. In the study by Guenther *et al.* (1991), the cuvette was clamped directly onto the surface of a Eucalyptus leaf and a large increase in monoterpene emissions was observed just after clamping the leaf in the cuvette. The effects of clamping did not appear to influence isoprene emission rates. Although monoterpene emission rates stabilized after several hours, it was uncertain whether they fell back to levels which would occur from an undisturbed leaf. In spite of the warning by these authors that the monoterpene emission rates obtained in this way may not be representative of undisturbed leaves, their emission rate measurements for Eucalyptus have been utilized by subsequent researchers (e.g. Tanner *et al.* 1992).

The use of enclosure methodologies to measure biogenic NMOC emission rates involves inherent problems which may limit their reliability. As mentioned above, rough handling of a plant has been shown to enhance monoterpene emissions from some plant species, especially herbaceous and shrubby species which store monoterpenes in externally located glandular trichomes (Arey, *et al.*, 1995). Thus, the process of enclosing the plant for measurement experiments may result in inflated emission rate estimates due to rough handling. On the other hand, plants in the field are routinely disturbed by the effects of wind and animals (e.g. birds, squirrels, etc.). Note, however, that Juuti *et al.* (1990) did not observe any significant effect on "stirring" the air within the enclosure with a portable fan, whereas "rough handling" increased the emission rate by an order of magnitude or more. Further quantification of effects associated with the handling of plants during emission rate measurements involving enclosure is needed.

A second problem associated with enclosure methods is the availability of nutrients. Studies have shown (see section 4.3) that conditions of nutrient stress can alter NMOC emission rates from some plant species. This problem is of particular concern for natural plant species since emission rate measurements taken for plants grown in greenhouses or in fields with ample water and nutrient supplies may not be representative of plants in the wild.

Another problem associated with enclosure studies (as well as other measurement methods) are seasonal variation in emissions. Emission measurements are typically performed over the course of a single day or a few days. As a result, the measured emission rate represents a "snap-shot" in time and may not be representative of emission rates at different times of the year.

A final problem common to most studies conducted on biogenic emissions concerns the lack of reporting of the full range of measurement conditions (assuming they were obtained in the first place). In many past studies, not all relevant environmental conditions under which measurements were made were reported. Often, researchers have simply applied an emission rate correction algorithm to the raw data to normalize them to a standard set of conditions. In many cases, this deficiency makes it impossible to re-correct emission rates with more refined and extensive correction algorithms as they are developed.

4.6.2 Ambient Measurement Methods

Due to the inherent problems associated with enclosure methods to determine biogenic NMOC emission rates, two additional methods have been employed. These were tracer studies (Arnts *et al.*, 1982; Lamb *et al.*, 1986) and micrometeorological gradient studies (Knoerr and Mowry, 1981; Lamb *et al.*, 1985). One advantage these two methods have over enclosure studies is they do not result in disturbance of the plant during measurement. Another advantage is they may be more representative of actual emission rates since the plants are generally growing in their natural habitat.

Micrometeorological gradient studies are performed by determining biogenic NMOC concentrations at varying heights above a forest canopy using sampling instruments positioned on a tall tower. In addition to NMOC sampling, vertical and horizontal diffusivities, wind speeds and directions, and temperatures are measured at the various heights to account for dispersion and

transport. After also taking into account reaction with atmospheric oxidants (e.g. OH, NO_3, and O_3), total emission fluxes can be estimated. By applying appropriate biomass factors, emission rates per plant or per dry weight leaf biomass can then be determined.

Tracer studies have an advantage over micrometeorological gradient methods in not relying on precise gradient measurements (Lamb *et al.*, 1986). In this methodology, a tracer (sulfur hexafluoride) was released at a known and steady rate at several points within the region of study. Using the results of subsequent ambient measurements of the tracer and NMOC concentration downwind of the release point, and taking into account dispersion of the tracer plume and degradation of the NMOC by atmospheric oxidants, total emission rates can be back-calculated using Gaussian atmospheric dispersion algorithms. As with the gradient method described above, once the total emissions are determined, emissions per plant or per dry weight leaf mass can be estimated by applying appropriate biomass factors.

A major problem with these types of measurements is the requirement for a homogeneous plant species distribution. Canopy measurements work best for large forest stands consisting of a single tree type, or at most two or three tree species. In regions with wide habitat diversities, such as California's San Joaquin Valley and South Coast air basins, emission measurements made in one region by these methods in general will not be representative of emissions from other regions with different plant species distributions. Thus, studies would have to be performed at a wide variety of locations which would be prohibitively expensive. As a result of these limitations, canopy studies have usually been applied to homogeneous forest stands. Finally, as with enclosure methods, canopy measurements only represent a "snap-shot" in time and may not be representative of emission rates at other times of the year.

4.7 Assignment of Emission Rates to Non-Measured Plant Species

Of the more than 400 plant species currently identified in the SoCAB (Horie *et al.*, 1990), experimental emission rate measurements have been performed on only about twenty percent. In recent years, relatively few new emission rate measurements have been performed, and there is little measurement research currently underway in California. Due to budget constraints and the laborious nature of such measurements, this situation is unlikely to change in the near future. As a result, in order to compile biogenic hydrocarbon emission inventories, there exists a need

to develop methodologies for assigning emission rates to those plant species for which no measured data are available.

Benjamin *et al.* (1996b) described such a methodology based on taxonomic relationships at the genus and family level. The foundation of this methodology lies in the premise that closely related plant species are more likely to have similar emission rates and NMOC compositions than more distantly related species. This premise is supported by phytochemical research by Siegler (1981), and Charlwood and Charlwood (1991), who found similarities in terpene production and storage between closely related plant species. In addition, Ross and Sombrero (1991) found evidence that a predominance of monoterpene emitters were from plant families native to Mediterranean climates.

In the approach of Benjamin *et al.* (1996b), the assignment of an emission rate to a particular plant species was based on the average emissions by related plant species at the lowest possible organization level (i.e. genus level being the best, followed by family level). As a result, of the 372 tree and shrub species listed in Benjamin *et al.* (1996b), 33% of the assigned emission rates were based on direct measurement, 32% were based on relationships at the genus level, and 21% were based on relationships at the family level. For those plant species for which no related species at or below the family level could be found with directly measured rates, no emission rate was assigned. This applied to the remaining 14% of the species identified in Benjamin *et al.* (1996b).

Emission rate estimates were based only on isoprene and monoterpene emissions due to the lack of data on other organic compounds which have been shown to be emitted from vegetation (Winer *et al.* 1989, 1992). Horie *et al.* (1991) used a similar procedure to assign emission rates to non-measured species, however these authors used the median value for a given plant genus or family to assign an emission rate rather than the average value used by Benjamin and co-workers. At the present time, due to the small number of species for which direct measurements have been performed, no comparative analysis can be performed to establish whether median or average values provide a more reliable assignment.

At the present time, taxonomic relationships appear to provide both a cost-effective and time-effective method for assigning emission rates to non-measured plant species given the lack of direct measurements of NMOC emissions for many plant species found in California's air

basins. However, the strengths and limitations of this methodology needs to be recognized. In comparing emission rates from plant species of the same genus, Benjamin *et al.* (1995b) found that most tree species within the same genus exhibited emission rates which differed by a factor of ten or less (e.g. *Acer*, *Schinus*, *Picea*, *Pittosporum*, and *Platanus*). While many tree species within the same family also exhibited emissions which differed by less than a factor of ten (e.g. *Anacardiaceae*, *Cornacea*, *Cupressacea, Juglandace*a, and *Magnoliacea*), emission rates for species within the family *Arecaceae*, for example, differed by as much as a factor of thirty-two, indicating that family level assignment of emission rates involves a greater level of uncertainty.

On the other hand, given that emission rates across all families listed in the study varied by over four orders of magnitude, the taxonomic approach appears to provide a satisfactory first order approximation of NMOC emission rates. However, as noted by Benjamin *et al.* (1995b), the reliability of the taxonomic method for assigning emission rates to non-measured plant species can be improved by performing additional emission rate measurements, especially on plant species from families and genus' in which few measurements have been performed to date. Another recommendation is that future direct measurements be performed on those plant species with the largest biomasses in a given airshed and those which have either very high or very low emission rates assigned on the basis of the taxonomic method. This would not only provide additional data which can be used to obtain greater reliability in further application of the taxonomic method, but will also reduce overall uncertainties in the generation of future biogenic emission inventories.

4.8 Algorithms for Emission Rate Variability

As discussed earlier, emission rates of isoprene and monoterpenes are known to depend on many environmental parameters, including temperature, light intensity, relative humidity, and ambient CO_2 levels (Tingey *et al.*, 1979, 1980, 1981; Monson and Fall, 1989, Juuti *et al.*, 1990; Guenther *et al.*, 1991, 1993). In order to normalize emission rates to common conditions (e.g. standard temperature), and to use numerical computer models to evaluate the influence of vegetation on ambient air quality, algorithms have been developed to describe variations in hydrocarbon emissions by vegetation as a function of these environmental parameters. This

section presents these algorithms separately for isoprene and monoterpenes, describes the history of their development and discusses their strengths and limitations.

The general structure of algorithms used to model biogenic emission rates for various environmental conditions takes the form:

$$\mathbf{ER = ER^{\circ} \times EF} \qquad \textbf{(4-1)}$$

where ER ("specific emission rate") is the hydrocarbon emission rate at any set of environmental conditions in μg hydrocarbon/g (dry leaf biomass)/hr, ER° ("normalized emission rate") is the emission rate at a pre-defined set of environmental conditions (usually 30° C and saturating light conditions (>800 $\mu E/m^2/hr$)), and EF ("environmental factor") is a modifying factor dependent upon the environmental conditions.

The environmental factor is generally obtained from a complex algorithm which has evolved over the past 15 years due to improved knowledge of the influence of environmental conditions on emission rates and from emission measurements for an increasing number of plant species. As a result of this evolution, biogenic emission inventories compiled over this 15 year time period may include different emission rates for a given vegetation species, even for the same set of environmental conditions.

A major cause of variation in environmental factors is that different hydrocarbon species have been shown to have different dependencies on environmental conditions (Tingey *et al.*, 1979, 1980; Guenther *et al.*, 1991, 1993). The most obvious example is that isoprene emission is known to be dependent on both light and temperature while monoterpene emissions are only temperature dependent (with one recent exception reported by Staudt and Seufert, 1995). Therefore, historically, two sets of algorithms have been developed for modeling these emission rates, one for isoprene and the other for monoterpenes.

As briefly noted above, emission rate algorithms are applied in two different manners. One is to normalize the emission rates. This involves taking emission rate data obtained under "field conditions" and normalizing them to a pre-defined specific set of standard conditions commonly employed in reporting such measurements in the literature. The second use is to convert the normalized emission rates to any desired set of environmental conditions. This

second use is generally made in numerical computer models. The following discussion describes the evolution of the algorithms used for isoprene and monoterpene emissions. The algorithms are presented in the form used to normalize emission rates to standard conditions from the original values obtained under experimental conditions.

4.8.1 Isoprene Emission Algorithms

An early attempt to model isoprene emission rate variability due to environmental influences was published by Tingey *et al.* (1979). This algorithm was based on emission data from Live Oak (*Quercus virginiana*) and was generally used to compile biogenic emission inventories prior to 1991. The algorithm took the form

$$ER^{\circ}(@30^{\circ}C) = \frac{(ER)\times(34.194)}{\exp\left[\frac{4.88}{1+\exp[-0.18\times(Temp.^{\circ}C-25.26)]}+0.11\right]} \qquad \textbf{(4-2)}$$

where ER° is the normalized emission rate, ER is the measured isoprene emission rate, and "Temp. °C" is the temperature at which the emission rate measurement was performed.

The primary deficiency of the Tingey algorithm was the failure to adequately account for variation in light intensities. The algorithm implicitely assumed measurement of the isoprene emission rate was performed at saturating light conditions (>800 $\mu E/m^2/hr$). However, when modeling diurnal fluctuations in emission rates using numerical computer models, there are times when light intensities are not saturating, specifically in the late evening, at night, and in the early morning. To account for the absence of light at night, it was assumed isoprene emission rates were essentially zero and, based on experimental evidence, this assumption appears to be valid. This still left an inability to account for isoprene emissions at low light intensities in the early morning and late evening hours.

To correct this deficiency, Pierce *et al.* (1990) modified the Tingey algorithm to include factors for varying temperatures and light intensities. This algorithm took the form

$$ER°(@30°C) = \frac{ER \times e}{10^P} \qquad (4\text{-}3)$$

$$\text{where } P = \left[\frac{a}{1+\exp[-b \times (Temp.°C - c)]}\right] - d$$

where ER° is the normalized isoprene emission rate, ER is the measured emission rate, and "Temp. °C" is the temperature at which the emission rate was measured. The coefficients a, b, c, and d are empirical constants which depend on light intensity.

Based on the experimental data for Live Oak from Tingey *et al.* (1981), Pierce reported the values shown below for these empirical coefficients.

Table 4-4. Reported empirical coefficients for Live Oak (Tingey *et al.*, 1981; Pierce *et al.*, 1990).

Light Intensity ($\mu E/m^2/s$)	Empirical Coefficients				
	a	b	c	d	e
800	1.200	0.400	28.30	0.796	1.00
400	0.916	0.239	29.93	0.462	1.95
200	0.615	0.696	32.79	0.077	4.75
100	0.437	0.312	31.75	0.160	10.73

The Tingey/Pierce algorithm was incorporated into the Biogenic Emissions Inventory System (BEIS) model developed by the U.S. EPA (Pierce *et al.*, 1990).

A major problem with the Tingey and Pierce algorithms was their description of the functional dependence on temperature of emission rates at high environmental temperatures. The algorithms showed the isoprene emission rate increasing with temperature to approximately 35-40° C where emissions leveled off and became constant with temperature (see Figure 4.2). However,

more recent experimental evidence (Guenther *et al.*, 1991) indicate isoprene emission rates increase only until approximately 35° C and then decline with higher temperatures.

Based on these observations, a new algorithm was developed by Guenther *et al.* (1991) using data from a single species of eucalyptus (*Eucalyptus globulus*). In addition to structuring the algorithm to account for the decreasing emission rates at higher temperatures, the Guenther algorithm, for the first time, included factors for relative humidity and ambient CO_2 concentration.

The Guenther *et al.* (1991) algorithm took the form

$$ER^{o}(@30^{o}C) = \frac{ER}{H \cdot C \cdot L \cdot T} \qquad \textbf{(4-4)}$$

where: **ER**^{o} is the mean normalized isoprene emission rate
ER is the measured isoprene emission rate
H is the correction factor for humidity
C is the correction factor for ambient CO_2 concentration
L is the correction factor for light intensity
T is the correction factor for temperature

Each of the four correction factors represent equations (presented below) that determine the effect that factor has on the overall emission rate.

Humidity

$$H = RH(H_1) + H_2 \qquad \textbf{(4-5)}$$

where: **H** is the correction factor for humidity
RH is the relative humidity (%)
$\mathbf{H_1}$ = 0.00236
$\mathbf{H_2}$ = 0.8495

Carbon Dioxide Levels

$$C=[CO_2]C_1 + C_2 \tag{4-6}$$

where: **C** is the correction factor for CO_2 concentration
[CO_2] is the CO_2 mixing ratio (ppm)
C_1 = 0.00195 for $[CO_2] < 100$
= 0 for $100 < [CO_2] < 600$
= -0.0041 for $[CO_2] > 600$

C_2 = 0.805 for $[CO_2] < 100$
= 1 for $100 < [CO_2] > 600$
= 1.28 for $[CO_2] > 600$

Light Intensity

$$L = \frac{x - \sqrt{x^2 - 4f \cdot I \cdot L}}{2L_1} \qquad x = f \cdot I + L_1 + L_2 \tag{4-7}$$

where: **L** is the correction factor for light intensity
f is the fraction of light absorbed by the chloroplast (0.385)
I is the irradiance ($\mu E/m^2/s$)
L_1 = 105.6
L_2 = 6.12

Temperature

$$T = \frac{\exp\left[\frac{T_1(T_L - T_S)}{RT_LT_S}\right]}{1 + \exp\left[\frac{T_2(T_L - T_3)}{RT_LT_S}\right]} \tag{4-8}$$

where: T is the correction factor for temperature
T_L is the leaf temperature in Kelvin
T_S is the normalizing temperature
R is the gas constant (8.314 J/K/mol)
T_1 = 95100 J/mol
T_2 = 231000 J/mol
T_3 = 311.83

This algorithm was considered superior to the Tingey and Pierce algorithms and was subsequently adopted in the development of biogenic emission inventories (for example Benjamin *et al.*, 1996a).

Recently, Guenther and co-workers (Guenther *et al.*, 1993) have published modification of their earlier algorithm based on studies of Eucalyptus (*Eucalyptus globulus*) and three additional plant species: Sweet gum (*Liquidambar stryaciflua*), Aspen (*Populus tremuloides*), and Velvet bean (*Mucuna pruriens*). This modified version of the Guenther *et al.* (1991) algorithm excludes corrections for relative humidity and CO_2 levels since these factors appear to have small or negligible effects on calculated emission rates. In addition, few if any of the studies reporting hydrocarbon emission rates for vegetation include these parameters and numerical computer models used to determine the air pollution effects of hydrocarbon emissions from plants rarely have provisions for this type of information.

The modified Guenther *et al.* (1993) algorithm for isoprene emission is given by

$$ER^{o}(@30^{o}C)=\frac{ER}{C_L \cdot C_T} \qquad \textbf{(4-9)}$$

where: $\mathbf{ER^{o}}$ is the mean normalized isoprene emission rate
ER is the measured isoprene emission rate
$\mathbf{C_L}$ is the correction factor for light intensity
$\mathbf{C_T}$ is the correction factor for temperature

As with the earlier version (Guenther *et al.*, 1991), the two correction factors represent equations (presented below) that determine the effect that factor has on the overall emission rate.

Light Intensity

$$C_L = \frac{\alpha \cdot C_{LI} \cdot L}{\sqrt{1+\alpha^2 \cdot L^2}} \qquad \textbf{(4-10)}$$

where: C_L is the correction factor for light intensity
L is the irradiance ($\mu E/m^2/s$)
C_{L1} is an empirical coefficient (= 1.066)
α is an empirical coefficient (= 0.0027)

Temperature

$$C_T = \frac{\exp\left[\frac{C_{T1}(T-T_S)}{R \cdot T_S \cdot T}\right]}{1+\exp\left[\frac{C_{T2}(T-T_M)}{R \cdot T_S \cdot T}\right]} \qquad \textbf{(4-11)}$$

where: C_T is the correction factor for temperature
T is the leaf temperature in Kelvin
R is the gas constant (8.314 J/K/mol)
T_S is the normalizing temperature
T_M is an empirical constant (= 314 K)
C_{T1} is an empirical constant (= 95,000 J/mol)
C_{T2} is an empirical constant (= 230,000 J/mol)

Using data from the four plant species employed to construct the 1993 version of the algorithm, Guenther and co-workers performed a sensitivity analysis to calculate how well each of the previous algorithms modeled measured hydrocarbon emissions. In this analysis, it was found the Guenther *et al.* (1993) algorithm best correlated with the experimental data, being able to account for about 90% of observed diurnal variability and to predict diurnal variations in hourly averaged isoprene emissions to within 35%. Based on this analysis, it is recommended this most recent algorithm be used in numerical computer models.

A problem arises when attempting to use either of the Guenther algorithms to compile biogenic hydrocarbon emission inventories. As noted earlier, many published studies reporting measured hydrocarbon emission rates from vegetation did not include the raw data. Instead, emission rates were generally presented as normalized to either 28° C or 30°C. As a result, attempts to compile (or recompile) inventories using the most recent Guenther algorithm (the 1993 version) by re-normalizing the original emission rates are made difficult or impossible

because for at least certain plant species, the initial data are not available in the published literature.

This problem can be handled in a number of ways. For example, Bloch and Winer (1993) used the Tingey *et al.* (1979) algorithm as modified by Pierce *et al.* (1990) to correct isoprene emission rates to 30°C at saturating light conditions, then used the Guenther *et al.* (1991) algorithm to estimate daily isoprene emission rates. The problem with using this approach is that the two algorithms model isoprene emissions differently. For the same set of raw data, the Tingey/Pierce algorithm will predict an isoprene emission rate at normalized conditions different from that predicted by the Guenther *et al.* (1993) algorithm. This effect is more pronounced as the environmental conditions used during the measurement process deviate from the normalized conditions (i.e. the greater the difference between actual measurement conditions and normalized conditions, the greater the difference between predicted emission rates using the Tingey/Pierce versus the Guenther algorithm). The recommended approach is to use the Guenther *et al.* (1993) algorithm to normalize emission rates from raw data when available, and to use the normalized emission rates as corrected by the Tingey *et al.* (1979) or Pierce *et al.* (1990) algorithms from earlier studies when the raw data were not given. While this is not a perfect solution, it is the best that can be done using currently available data.

4.8.2 Monoterpene Emission Algorithms

Algorithms modeling monoterpene emissions have followed the same structural evolution as the algorithms modeling isoprene emission rates. As with isoprene emission algorithms, the first attempt to model monoterpene emissions was made by Tingey *et al.* (1980). As the state of knowledge regarding monoterpene emissions improved, the algorithms subsequently improved, resulting in modifications of the algorithm by Pierce *et al.* (1990), Guenther *et al.* (1991), and Guenther *et al.* (1993). However, the evolution in the algorithm for monoterpenes produced significantly less change in calculated emission rates compared to changes resulting from modifications to the isoprene emission rate algorithm over time.

The dependence of monoterpene emissions on many environmental factors has been investigated, including leaf temperature (Dement *et al.*, 1975; Tingey *et al.*, 1980; Juuti *et al.*,

1990; Guenther *et al.*, 1991), relative humidity (Dement *et al.*, 1975), foliar moisture (Lamb *et al.*, 1985), and light intensity (Steinbrecher *et al.*, 1988). Leaf temperature is currently believed to play the greatest role in controlling monoterpene emission rates. Investigations have shown emissions are controlled primarily by the vapor pressure and pool size of the specific monoterpene (Dement *et al.*, 1975). This conclusion was supported by data from Lamb *et al.* (1985) who found the temperature dependence of monoterpene emissions was similar in living and non-living plants. This finding indicated short-term monoterpene emission variability does not depend significantly on the physiological processes of the plant, but rather on the physical properties of monoterpenes. However, physiological processes may influence long-term variability by controlling the size of the leaf monoterpene pool. For plants which have been studied, relative humidity, foliar moisture, and light intensity have been found to have a negligible impact on monoterpene emissions in comparison to the impact of leaf temperature (Tingey, 1981; Juuti *et al.*, 1990; Guenther *et al.*, 1991), and therefore these factors have been omitted from current monoterpene emission rate algorithms.

The first attempt to model monoterpene emission rates was published by Tingey *et al.* (1980) from data obtained from Slash Pine (*Pinus elliottii* Engelm) and took the form

$$ER^{o}\ (@30^{o}C) = \frac{ER \times 6.392}{\exp[a + b(Temp.^{o}C)]} \qquad (4\text{-}12)$$

where ER^{o} is the normalized emission rate, ER is the measured isoprene emission rate, Temp. °C is the temperature at which the emission rate measurement was performed, and a and b were empirical coefficients which depended on the specific monoterpene emitted. The values of a and b were given as shown in the table below.

Table 4-5. Empirical coefficients for selected monoterpenes (Tingey *et al.*, 1980; Pierce *et al.*, 1990).

	Empirical Coefficient	
Compound	a	b
α-pinene	-0.850	0.0670
β-pinene	-1.458	0.0769
Myrcene	-3.803	0.0764
Limonene	-4.450	0.0742
β-Phellandrene	-3.790	0.0652
$\sum$ Monoterpenes	-0.332	0.0729

Applications of the Tingey algorithm for the construction of biogenic emission inventories have used average values of a and b for the sum of monoterpenes. This is because most published measurements failed to separate individual monoterpene species, reporting either the sum of all monoterpene species or the sum of all terpene species (which included sesquiterpene compounds).

Pierce *et al.* (1990) published a modified algorithm for monoterpene emissions which differed from the Tingey algorithm and took the form

$$ER^{o}\ (@30^{o}C) = \frac{ER}{\exp[a(Temp.^{o}C - 30)]} \qquad (4\text{-}13)$$

where ER° is the normalized emission rate, ER is the measured emission rate, Temp. °C is the temperature at which the emission rate was measured, and "a" is an empirical coefficient which depends on the monoterpene species emitted (0.67 for α-pinene, and 0.739 for monoterpenes in general). While the two algorithms used the same empirical constant for α-pinene emissions, different values were given for monoterpene emissions in general. Pierce *et al.* (1990) did not provide any justification for modifying the empirical constant for monoterpene emissions, citing

only the original articles from which the Tingey algorithm was derived (i.e. Tingey *et al.*, 1980 and Tingey *et al.*, 1981).

Guenther *et al.* (1991) published an additional algorithm based on studies from Eucalyptus (Eucalyptus globulus) that took the form

$$ER^{o}\ (@30^{o}C) = \frac{ER}{\exp(T_L \cdot M_1 + M_2)} \qquad \textbf{(4-14)}$$

where: **ER°** is the mean normalized monoterpene emission rate
ER is the measured monoterpene emission rate
$\mathbf{T_L}$ is the leaf temperature (Kelvin)
$\mathbf{M_1}$ is an empirical coefficient
= 0.100 for α-pinene
= 0.094 for cineole
$\mathbf{M_2}$ is an empirical coefficient
= -30.212 for α-pinene
= -28.318 for cineole

This algorithm was further modified by Guenther *et al.* (1993) using additional data obtained from published literature and took the form

$$ER^{o}\ (@30^{o}C) = \frac{ER}{\exp[\beta \cdot (T - T_S)]} \qquad \textbf{(4-15)}$$

where **ER°** is the mean normalized monoterpene emission rate
ER is the measured monoterpene emission rate
T is the measured monoterpene emission rate temperature
$\mathbf{T_S}$ is the normalizing temperature (in this case, 303 K)
β is an empirical coefficient (recommended value = 0.09 K^{-1})

The value of β determines the temperature dependence of the monoterpene emission rate and was estimated using data obtained from published literature. As shown in Table 4-6, the values of

Table 4-6. Estimates of coefficient β (K^{-1}) which defines temperature dependence of monoterpene emission rates (modified from Guenther *et al.*, 1991)

Monoterpene	Vegetation Species	β (K^{-1})	Reference
α-pinene	Abies concolor	0.144	Rasmussen (1972)
	Pinus strobus	0.110	Rasmussen (1972)
	Pinus taeda	0.139	Rasmussen (1972)
	Pinus ponderosa	0.099	Rasmussen (1972)
	Pinus elliottii	0.091	Arnts et al (1978)
	Pinus elliottii	0.067	Tingey (1981)
	Pinus densiflora	0.108	Yokouchi and Ambe (1984)
	Pinus sitchensis	0.100	Evans et al (1985)
	Picea engelmannii	0.114	Evans et al (1985)
	Various	0.131	Lamb et al (1987)
	Pinus radiata	0.085	Juuti et al (1990)
	Eucalyptus globulus	0.094	Guenther et al (1991)
	Pinus taeda	0.089	Guenther et al (1993)
	Average:	0.105 (± 0.022)	
β-pinene	Pinus elliottii	0.077	Tingey (1981)
	Picea sitchensis	0.085	Evans et al (1985)
	Picea engelmannii	0.112	Evans et al (1985)
	Pinus taeda	0.092	Guenther et al (1993)
	Average:	0.0915 (± 0.015)	
camphor	Salvia mellifera	0.068*	Dement et al (1975)
	Salvia mellifera	0.120†	Dement et al (1975)
	Average:	0.094 (± 0.037)	
myrcene	Pinus elliottii	0.076	Tingey (1981)
	Picea sitchensis	0.062	Evans et al (1985)
	Picea engelmannii	0.057	Evans et al (1985)
limonene	Pinus elliottii	0.074	Tingey (1981)
	Average:	0.074	
β-phellandrene	Pinus elliottii	0.065	Tingey (1981)
	Pinus engelmannii	0.079	Evans et al (1985)
	Average:	0.072 (± 0.010)	
camphene	Picea sitchensis	0.067	Evans et al (1985)
	Picea engelmannii	0.077	Evans et al (1985)
	Average:	0.072 (± 0.007)	
Totals	Overall Average:	0.092 (± 0.023)	

* Branch kept at a temperature of 10° C before measurement.
† Branch kept at a temperature of 40° C before measurement.

β range from 0.057 to 0.114 with an average of 0.092 ($\pm$ 0.023). Although individual monoterpenes exhibit different values of β, these differences were not statistically significant due to the large variance in the empirically derived values. Therefore, Guenther *et al.* (1993) recommend a single value of 0.09 (K^{-1}) for β for all monoterpene species when using the algorithm. This selection is consistent with recent studies (Arey *et al.*, 1995; Geron *et al.*, 1994).

4.8.3 Leaf Canopy Correction

In forested areas, all leaf biomass is not subject to the same environmental conditions throughout the canopy. While leaves in the upper canopy may receive direct sunlight, leaves in the lower canopy are expected to receive significantly reduced sunlight levels due to shading effects. Since isoprene emissions are directly correlated with light intensity, "canopy conditions" are expected to have a significant effect. In addition to attenuated light levels, leaf temperatures are expected to vary within the canopy. For example, it has been demonstrated that leaves subject to direct sunlight can be as much as 10 °C warmer than ambient temperatures (Gates, 1968). On the other hand, leaves in the lower portions of the canopy which do not receive direct sunlight may have temperatures lower than ambient.

To account for variations in environmental factors within a forest canopy, Lamb *et al.* (1993) developed a forest canopy model which was used to predict changes in sunlight, temperature, humidity, and windspeed as a function of height. Using this model, environmental conditions at various heights within the canopy were predicted based on data obtained from above the canopy measurements or from local meteorological records. Using these stratified conditions, leaf temperatures within each level were estimated using an empirical leaf energy balance algorithm based on wind tunnel studies (Gates, 1962, 1968; Gates and Papain, 1971).

Lamb *et al.* (1993) applied this canopy model to both coniferous and deciduous forests in an effort to predict biogenic NMOC emission rates. Using idealized, homogeneous forest characteristics of canopy height (20 meters for coniferous forests and 15 meters for deciduous forests), estimated vertical biomass distribution, and leaf orientation, shape, and size, the canopy model yielded a 50% reduction in isoprene emissions, while terpene emissions were reduced by 6%. These results suggest the importance of accounting for attenuation of light intensity due to

canopy effects, particularly for isoprene emissions. This algorithm was incorporated into the PC-BEIS, UAM-BEIS, and GEMAP biogenic inventory models (see Section 6.3.3.1.2).

Geron *et al.* (1994) developed an alternate canopy model to account for the attenuation of solar radiation at lower levels within the forest canopy. Leaf temperatures were neglected in this model based on the above noted evidence obtained by Lamb *et al.* (1993) that leaf temperature variations had only a minor effect on biogenic NMOC emission rates. This model differs from the one derived by Lamb *et al.* (1993) in several respects, including standardized emission rates, forest composition, vertical variations of environmental parameters within the canopy, and environmental correction algorithms. When biogenic inventories for selected forest sites using the BEIS model were compared to the model developed by Geron *et al.* (1994), the results suggested the BEIS model underestimated isoprene emissions by a factor of between 5 and 10 while terpene emission estimates from the two models were comparable.

The use of these canopy models to correct for variations in environmental conditions at various heights within the canopy are viewed as important advancements in the characterization and quantification of biogenic NMOC emission rates. However, their applicability to the SJVAB and SoCA, as well as many other airsheds in California, is questionable. While the attenuation of solar radiation within various vegetative communities needs to be correctly accounted for, the characteristics of these California land use regions are quite different from those for which the canopy models were developed and applied. Specifically, the models have been developed and applied to homogeneous forest communities with species compositions consisting of only a few types of trees. This is not the case in either the SJVAB or the SoCAB where the plant communities are much more diverse. Clearly, there are both a much greater number of plant types and more complex community structure in these air basins. As a result, the effects of shading on isoprene emission rates from different plant species within these regions may not be accurately predicted by current canopy models developed for southern, northeast and northwest forests. Secondly, the plant densities in many of the vegetative communities in the SJVAB and SoCAB are not as high as in the regions for which the models were developed. As a result, significantly more leaf surface will be subject to direct sunlight in these airsheds than in forest communities.

Using a canopy shading model developed by the U.S. EPA, the South Coast Air Quality Management District (1991) estimated that canopy shading effects decrease SoCAB biogenic emissions by an average of 23%. This reduction factor was subsequently employed in the biogenic inventory estimates by Causley and Wilson (1991) and Benjamin *et al.* (1995a). Use of this correction factor is viewed as highly simplistic, however, and needs further evaluation. In particular, different isolated tree and shrub species are expected to have different emission rate reductions from canopy shading effects due to the different structural characteristics of many plant species. Investigations are therefore needed to provide better estimates of emission rate reductions due to canopy shading effects for specific tree and shrub species with characteristic morphological (e.g. crown shape and volume) properties. While it is understood that determination of canopy shading factors for each individual species is too costly and time-consuming, we recommend canopy adjustment factors be developed for groups of species having similar structural characteristics.

In summary, because the canopy models discussed above may not be appropriate and/or may be too simplistic to provide reliable emission rate reduction estimates for the vegetation communities found in California, improved methodologies need to be developed to account for canopy shading effects. Until such improved estimates are obtained, significant uncertainties in total biogenic emission inventories may persist.

4.8.4 Summary

Algorithms for biogenic emission rates have changed over the past 15 years due to improved knowledge of factors influencing emission rates, and from emission measurements for an increasing number of plant species. Based on analysis of their ability to model actual emission rates measured under varying environmental conditions, it is recommended the algorithms of Guenther *et al.* (1993) be used to compile biogenic emission inventories and in numerical computer models.

In compiling biogenic emission inventories, however, a number of problems arise in applying current emission rate algorithms. First, most published emission rate measurements did not include reference to the specific light intensity falling on the plants at the time of the measurement. As a default, it is therefore generally assumed the light intensity was saturating

at the time of the measurement. While this assumption may often be valid, even during partially cloudy days the available light intensity should be greater than 800 uE/m^2/s, there are times when the light intensity is not saturating, particularly in the early morning and late evening (and obviously at nighttime). Second, it is important the same algorithm be applied when normalizing emission rates to a standard set of environmental conditions as when using the normalized emission rates to estimate diurnal variations. Use of different algorithms to normalize emission rates and to estimate emission variability will lead to increased uncertainty in emission inventory estimates.

With respect to algorithms used for leaf canopy corrections, it is unlikely the Lamb *et al.* (1993) or the Geron et al. (1994) methodology for homogeneous forests can be applied to the SoCAB and SJVAB. At present, the SCAQMD's reduction factor of 23% remains the best approach for the plant species distributions found in these airsheds, while recognizing this is a simplistic approximation. Clearly, further investigation is needed to determine the appropriateness of these algorithms and correction factors for use in California's air basins in order to reduce the level of uncertainty biogenic emission inventory estimates.

4.9 NO_x Emissions from Soils

4.9.1 Introduction and Background

Nitrogen oxides ($NO + NO_2 = NO_x$) play a pivotal role in the troposphere in the formation of photochemical transformation products such as ozone and nitric acid. Emissions of NO_x occur due to both man-made (anthropogenic) and natural (biogenic) activities. An estimated annual NOx emission inventory for the United States from anthropogenic sources is shown in Table 4-7. The largest components of this inventory are transportation sources and electric utility emissions. Logan (1983) presented an emission inventory for the U.S. and Canada for both anthropogenic and non-anthropogenic sources (Table 4-8). In this inventory, fossil fuel combustion was the largest NO_x source, accounting for approximately 85% of the total NO_x budget, with natural sources (including lightning flashes, and soil microbial nitrification and denitrification) accounting for the other 15%. However, considerable uncertainty was associated with these estimates of the NO_x budgets. For example, Logan (1983) estimated that soils accounted for between 7% and 30% of the global total NO_x emissions. A high degree of uncertainty was also reported in studies

Table 4-7. Estimated annual U.S. NOx emissions from anthropogenic sources obtained from recent inventories.

Source Category	Emissions (teragrams of nitrogen/year)			
	NAPAP Inventory[a]	EPA Trends[b]	MSCET[c]	EPRI[d]
Electric utilities	1.8	2.1	1.9	2.2
Nonutility combustion	1.1	1.0	1.1	1.3
Transportation	2.4	2.7	2.3	2.4
Other sources	0.3	0.2	0.2	0.4
Total	5.6	6.0	5.5	6.3

[a]EPA, 1989.
[b]EPA, 1990b.
[c]MSCET, Month and State Current Emissions Trends, Kohout *et al.*, 1990.
[d]EPRI, Electric Power Research Institute, Heisler *et al.*, 1988. Amounts are for 1982. The other amounts presented in the table are for 1985.
Source: Placet *et al.*, 1990.

Table 4-8. Sources of NO_x in North America (from Logan, 1983).

	United States	Canada	Total
Biomass burning	0.05 - 0.15	0.025 - 0.075	0.08 - 0.23
Lightning	~ 0.3 (0.07 - 0.7)	~ 0.06 (0.015 -0.15)	~ 0.36 (0.09 - 0.9)
Microbial activity in soils[a]	~ 0.4 (.02 - 0.8)	~ 0.2 (0.1 - 0.4)	~0.6 (0.3 - 1.2)
Oxidation of ammonia[a]	0.0 - 0.1	0.0 - 0.05	0.0 - 0.15
Input from the stratosphere[a]	negligible	negligible	< 0.04
Subtotal	~ 0.8	~ 0.3	~ 1.1
Fossil fuel combustion[b]	5.8	0.6	6.4
Total	~ 6.6	~0.9	~ 7.5

Units: 10^{12} gm N yr^{-1}

[a] These estimates are based on the global estimates in Table 9, as discussed in the text.

[b] Taken from *U.S.- Canadian Memorandum of Intent* [1982a]. Logan estimated the reliability of anthropogenic emissions to be ±20%.

by Hahn and Crutzen (1982) and Stedman and Shetter (1983) who estimated that soils accounted for 0 to 29% and 13 to 50%, respectively, of total global NO_x. These results clearly indicate improved soil NO_x emission rate estimates are needed to better understand local, regional, and global contributions to the global NO_x budget.

While most biogenic emission inventories have focused on NMOC emissions, until recently little attention has been paid to biogenic sources of NO_x. However, recent evidence suggests NO_x (primarily as NO) emissions from soils have been underestimated in the past and therefore may play a significant role in local, regional, and global NO_x budgets (Aneja, 1994; Roselle, 1994; Valente and Thornton, 1993; Williams *et al.*, 1992; Williams and Fehsenfeld, 1991). For example, in a study of soil NO_x emissions from heavily fertilized agricultural soils in central Pennsylvania, Williams *et al.* (1988) reported NO release rates may be comparable (on a square meter per second basis) to those of urban areas. Although NO_x emissions from soils in urban regions are likely to be small or negligible in comparison to anthropogenic emissions of NO_x, the relative contribution of soil NO_x emissions in agricultural and rural regions may be significant due to lower levels of NO_x from combustion sources in such regions. Therefore, soil NO_x emissions in agricultural and rural regions could have implications concerning possible control strategies designed to limit ozone levels in such regions. If the level of NO_x emissions from soils turn out to comprise a substantial portion of the total budget in agricultural and rural regions, the efficacy of control strategies for NO_x emissions from anthropogenic sources could be reduced.

4.9.2 Microbial Processes

Nitrogen oxides from soils are produced by two major microbial processes: nitrification and denitrification (Aneja, 1994). Nitrification is the process where microbes in the soil aerobically oxidize ammonium (NH_4^+) ions to produce nitrites (NO_2^-) and nitrates (NO_3^-). During intermediate steps, NO_x compounds are produced and volatilize into the atmosphere. Denitrification is the process where microbes in the soil anaerobically convert nitrates into nitrogen (N_2) gas and nitrous oxide (N_2O). Again, during intermediate steps, NO_x compounds are produced and volatilize into the atmosphere.

At the present time, the question as to which of these two microbial methods contributes the greatest amount of NO_x compounds to the atmosphere is uncertain. However, recent emission rate measurements of NO_x compounds performed in California's Sierra foothills using the inhibitor acetylene have shown that NO production in soils used for cattle grazing and under oak canopies was due to nitrification processes (Davidson *et al.*, 1991). In addition, studies in Africa have indicated that NO_x emissions from soils under recently burned fields/vegetation were enhanced 10 to 100 times, likely due to increased quantities of NH_4^+ from field ashes (Levine *et al.*, 1990). Further investigation, however, is needed to determine the relative contribution of NO_x emissions from nitrification versus denitrification.

4.9.3 Measurements of NO_x Emission Rates

A number of studies have been performed measuring NO_x emission rates from a variety of different soil types from different regions of the world. Published values for these emission rates are shown in Table 4-9. As seen from these data, emission rates vary considerably depending upon location and land-use type. Agricultural fields appear to have the highest emissions, with corn fields having the highest emissions followed by grazed pasture lands. These high emission rates were believed to be due to high nitrogen content in the soils due to heavy fertilization and/or deposition of animal wastes (Valente and Thornton, 1993; Williams *et al.*, 1988; Anderson and Levine, 1987).

Emissions from grasslands appear to be of the same order of magnitude as agricultural soils. Besides salt marsh/estuarine regions, the lowest NO_x emitting soils are those of deciduous forests and ungrazed pastures. The higher emission rate values obtained by Valente and Thornton (1993) for the forest site were attributed to the presence of an adjacent grazing pasture where rainfall runoff was believed to cause higher nitrogen contents in the soils.

The utility of the emission rates reported in Table 4-9 remains limited at this time due to the large variability in the data. Within a given soil type, a wide range of emission rates have been reported. For example, cornfields in Tennessee and Pennsylvania were reported to have emission rates of 27 and 94 $ngN/m^2/s$, respectively. Also, mean NO emission rates from grasslands were shown to range from 0.77 to 10 $ngN/m^2/s$. Given the high variability in measured emission rates for different soil types, it is clear better methods need to be developed

Table 4-9. Reported NO emission rate measurements (modified and up-dated from Williams and Fehsenfeld, 1991)

Site Description and Location	Mean (Range) NO Emission (ngN m^{-2} s^{-1})	Reference
	Grasslands	
Ungrazed Pasture, Aspendale, Australia	1.6 (0.0 to 2.6)	Galbally and Roy (1978)
Meadow (bare soil), Finthen, Federal Republic of Germany	2.2 (-6 to 14.2)	Slemr and Seiler (1984)
Crested Wheat Grass, Erie, CO, U.S.A.	(-20 to 30)	Delany *et al.* (1986)
Grassland, Boulder, CO, U.S.A.	3.0 (0.028 to 65)	Williams *et al.* (1987)
Savanna (dry season) Guarico State, Venezuela	8 (3 to 15)	Johansson *et al.* (1988)
Savanna (rainy season), Guarico State, Venezuela	(9.5 to 117)	Johansson and Sanhueza (1988)
Chaparral (unburned), Southern California, U.S.A.	10 (0 to 35)	Anderson *et al.* (1988)
Shortgrass Prairie, Nunn, CO, U.S.A.	10.0 (1.15 to 52.9)	Williams and Fehsenfeld (1991)
Ungrazed Pasture, Sierra Foothills, CA, U.S.A.	0.77 (--)	Davidson *et al.* (1991)
Grazed Pasture, Sierra Foothills, CA, U.S.A.	2.77 (--)	Davidson *et al.* (1991)
	Coastal Marine	
Salt Marsh/Estuarine, North Inlet, SC, U.S.A.	0.03 (N.D. to 0.09)	Williams and Fehsenfeld (1991)
	Temperate Forests	
Coniferous Forest, Sorentorp, Sweden	0.35 (0.10 to 0.76)	Johansson (1984)
Coniferous Forest, Jaadras, Sweden	0.23 (0.10 to 0.56)	Johansson (1984)

Table 4-9. Reported NO emission rate measurements (modified and up-dated from Williams and Fehsenfeld, 1991) (continued).

Site Description and Location	Mean (Range) NO Emission ($ngN\ m^{-2}\ s^{-1}$)	Reference
	Temperate Forests	
Coniferous/Deciduous Forest, Scotia, PA, U.S.A.	1 (0.2 to 4.1)	Williams *et al.* (1988)
Deciduous Forest, Oak Ridge, TN, U.S.A.	0.3 (0.06 to 1.12)	Williams and Fehsenfeld (1991)
Deciduous Forest, Appalachian Mtns, NC, U.S.A.	0.13 (--)	Thornton and Valente (1992)
Deciduous Forest, Mississippi, U.S.A.	0.05 (--)	Thornton and Valente (1992)
Deciduous Forest, Pulaski/Lawrenceburg, TN, U.S.A.	Summer = 8.4 (--) Fall = 4.38 (--)	Valente and Thornton (1993)
	Agricultural	
Dairy Pasture Grazing Area, Edithvale, Australia	3.9 (2.2 to 5.9)	Galbally and Roy (1978)
Irrigated Grazing Pasture, Conargo, Australia	2.5 (--)	Galbally and Roy (1978)
Disused Cattle Milking Yard, Conargo, Australia	2.6 (1.5 to 3.7)	Galbally and Roy (1978)
Fertilized Agricultural Soils, Jamestown, VA, U.S.A.	6.6 (0.001 to 52.6)	Anderson and Levine (1987)
Unfertilized Agricultural Soils, Bennett, CO, U.S.A.	1.7 (0.001 to 16.3)	Anderson and Levine (1987)
Cornfield, Rockfield, PA, U.S.A.	94 (4.5 to 178)	Williams *et al.* (1988)
Wheatfield, Rockfield, PA, U.S.A.	1.2 (0.67 to 1.7)	Williams *et al.* (1988)
Fertilized Pasture, Tennessee, U.S.A.	Summer = 44.1 (--) Fall = 2.75 (--)	Valente and Thornton (1993)
Cornfield, Tennessee, U.S.A.	Summer = 27.0 (--) Fall = 2.85 (--)	Valente and Thornton (1993)

in order to be able to predict NO_x emission rates from a variety of soils in order to construct reliable emission inventories.

Using conservative emission rate estimates and techniques, Valente and Thornton (1993) scaled emission rate measurements from three different land use types (corn fields, pasture lands, and forests) to estimate the total contribution of soil NO_x in comparison to other sources for the entire state of Tennessee. The results of this estimation are shown in Figure 4-2. While it was acknowledged the three soil types were not likely to be representative of all soils types of the state of Tennessee, the calculation was believed to provide a rough estimate of the total contribution of NO_x from soil sources. The results of this estimation indicated that approximately 19% of the total NO_x budget for the state of Tennessee could be due to emissions from soils. This result suggests soil NO_x emissions should be included when conducting modeling studies for a region where extensive agricultural and rural land-use activities are occurring.

Local environmental conditions have been found to have significant effects on NO_x emission rates from soils. For example, factors such as temperature, soil type, nitrogen and moisture content, and soil pH have all been shown to affect NO_x emission rates. Soil temperature is an important controlling parameter due to its influence on biological reaction rates and soil gas diffusion rates (Williams *et al.*, 1992). Over the temperature range of 15-35 °C, NO_x emission rates have been observed to approximately double for every 10 °C increase in temperature, a fairly consistent result over a wide variety of sites (Williams *et al.*, 1992; Galbally, 1989; Haynes, 1986).

In the compilation of a NO_x emission inventory from soils in the United States, Williams *et al.* (1992) applied an algorithm, to account for the effects of temperature on soil NO_x emissions, which took the form

$$\textbf{NO emissions (ngN m}^{-2}\textbf{ s}^{-1}\textbf{) = A (ngN m}^{-2}\textbf{ s}^{-1}\textbf{) exp[(0.071 } \pm \textbf{ 0.007 °C}^{-1}\textbf{) T}_{soil}\textbf{ (°C)]} \qquad \textbf{(4-16)}$$

where A is a factor that was associated with the land use category. The value of A was dependent upon physical and chemical properties of the particular soil in question, including soil type, and soil nutrient and moisture levels. Other authors have developed similar algorithms

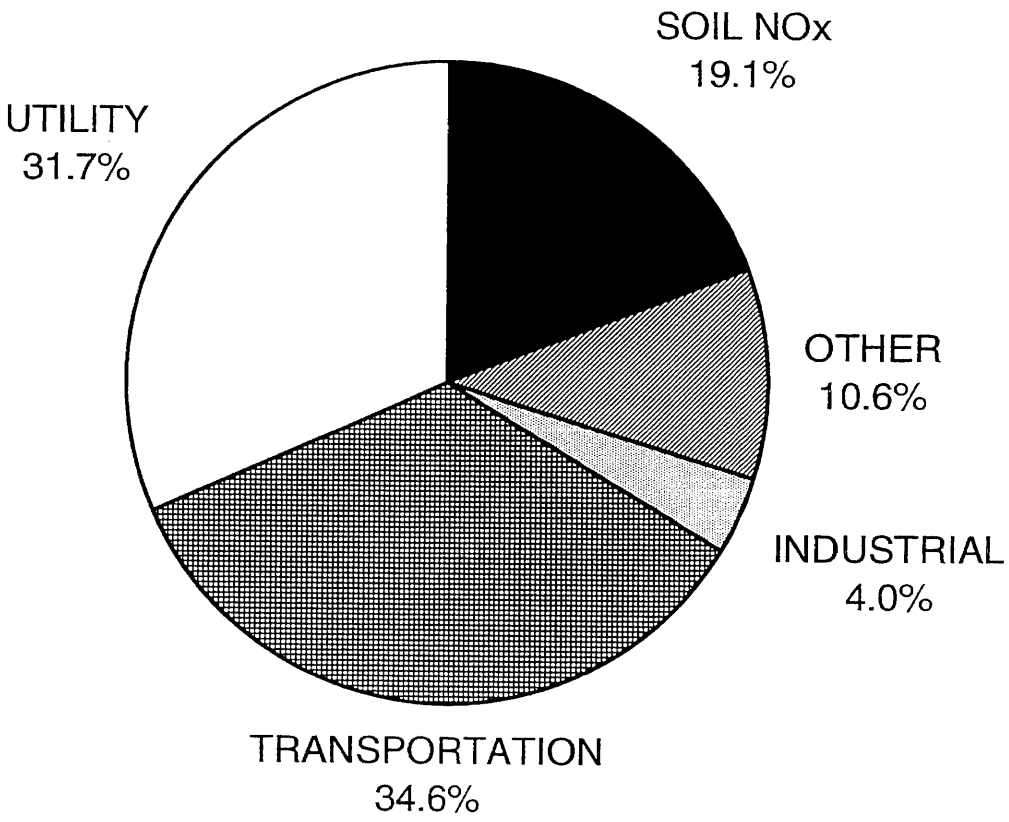

Figure 4-2. Comparison of summertime NOx emission for Tennessee, assuming that soil NO measurements at Giles County represent the entire state (from Valente and Thornton, 1993)

based on empirical evidence from specific soil types and regions. This temperature dependence is likely to play an influential role in NO_x emissions in the SJVAB due to high summertime soil temperatures.

Attempts to correlate NO_x emissions with other parameters have been less successful (Anderson and Levine, 1987;, Slemr and Seiler, 1991; Johansson *et al.*, 1988), likely due to the complexities involved in the production and emission of soil NO_x. For example, in studies of the linkage between N_2O production and emission, Jury *et al.* (1982) found that a substantial lag time of approximately 12 hours or more elapsed before steady state conditions were reached between N_2O production via denitrification and emission from the soil. Their analysis indicated a number of factors were involved in the attainment of steady state, including soil diffusion coefficient, location of gas production within the soil, and the storage capacity of the soil for a gas. Given the complexity of the soil, and the processes involved in the production and release of soil gases, it is understandable that accurate relationships have yet to be elucidated.

Given the data described here, it is recommended that for rural and agricultural areas NO_x emissions from soils should be included in modeling efforts to determine the effect of biogenic emissions on ambient air quality. This is especially true for the SJVAB where extensive agricultural activities occur. The influence, if any, of soil NO_x emissions in the SoCAB on observed ambient oxidant formation is much less certain given the enormous anthropogenic NO_x emission inventory. Although little of the land-use in the SoCAB is devoted to agricultural activities, emissions from soils in burn areas and areas where heavy fertilization is used (e.g. golf courses, home landscaping, etc.) may need to be assessed.

4.10 Critical Review of Inventories Relevant to California Air Basins

4.10.1 Winer *et al.*, 1983, South Coast Air Basin

4.10.1.1 Overview of Emission Factor Development

This study was performed for the California Air Resources Board in order to provide the first estimation of the contribution of biogenic hydrocarbons to the total hydrocarbon emission inventory for the SoCAB. Although it covered only a portion of the SoCAB, the study consisted of a comprehensive evaluation which included all necessary biogenic emission inventory factors including: (a) quantitative assessment of the area coverage of vegetation in randomly selected

sample areas within the SoCAB urban area, using a combination of high altitude (NASA U-2) and low altitude, high resolution, color infrared imagery; (b) field determination of the distribution and green leaf mass of the trees, shrubs, and ground covers found in the selected sample areas; and (c) experimental measurements of emission rates of isoprene and monoterpenes from the most abundant natural and ornamental species found in the SoCAB (Winer *et al.* 1983). Objectives (a) and (b) were discussed in Section 3.0 of the present report and will not be further discussed here. All emission rate factors used in the Winer *et al.* study were either directly measured or based on taxonomic relationships using data from emission rate measurements performed in the study. No emission rate factors from other studies were used to develop the inventory compiled in their report.

Direct measurement of emission rate factors were obtained by Winer *et al.* for 11 species of naturally occurring vegetation and 54 species of urban vegetation. The plant species classified as urban vegetation were further subdivided into 6 sub-classifications which included broad-leaf trees, conifers, flower and ground cover, grasses, palms, and shrubs. Since it was recognized that measurement of all plant species in the SoCAB would not be possible due to the enormous number of plant species types and time and resource limitations, selection of plants for direct measurement was based on their relative abundance in the study area (Miller and Winer, 1984). Only the most abundant plants in the study area were chosen for analysis. Experimental emission rate measurements were conducted on plant specimens at four different locations: Tanbark Flats in the San Gabriel mountains; Paramount Ranch in Agoura; Los Angeles State and County Arboretum in Arcadia; and greenhouses and the arboretum at U.C. Riverside. Tanbark Flats and Paramount Ranch were used for natural vegetation while the County Arboretum was used for ornamentals (except for a few species which were located on nearby streets). Grasses and groundcover species were grown in U.C. Riverside greenhouses.

Emission rate measurements were performed using enclosure techniques employing rigid PVC pipe-supported Teflon bags with GC-FID analysis of the chamber air samples (see section 4.6.1). A number of environmental conditions were recorded for each measurement and these were provided in the raw data, including chamber temperature, relative humidity, date and time of day of the emission rate measurement, and approximate sunlight exposure (expressed as either full or partial sunlight). The carbon dioxide concentration in the chamber atmosphere was

maintained at or near 360 ppm with a gas dilution system. Measurements of individual plant species were performed in triplicate. For each plant species measured, both raw emission rate data and normalized emission rate data (to 30 °C using the Tingey *et al.* (1979, 1980) algorithms for isoprene and monoterpenes) were reported. Although the steady state concentrations of the predominant monoterpene species in the chamber air were provided in the raw data, monoterpene emission rates for a given plant species were summed together and reported only as a single value. This was done to simplify any subsequent calculations since any adjustments for environmental conditions would be made using a single correction algorithm.

Since a large number of plant species were not measured but included in the overall inventory, assignment of surrogate emission factors had to be made. This assignment was based on emission rate measurements performed on plant species of the same genus. No mention was made concerning how an emission rate factor was assigned when more than one plant species of the same genus was measured directly.

In the construction of the final inventory, daytime emission rates from a single plant species was multiplied by 15 hours and summed with nighttime emission rates multiplied by 9 hours to obtain a per day estimate of total emissions by a given plant species. Daytime temperatures were assumed to be 30 °C while nighttime temperatures were assumed to be 25 °C. These temperature corrections were calculated using the Tingey *et al.* (1979, 1980) correction factors for isoprene and monoterpenes emission rate algorithms which were available at that time. Since isoprene emissions were known to fall essentially to zero at night due to the lack of solar radiation, these emissions were assigned as zero during these hours. Monoterpenes on the other hand, were known to be emitted at night and thus were assigned emission rates based on a temperature of 25 °C.

4.10.1.2 Review of Emission Factor Development

The experimental determination of emission rate factors was well thought out and utilized analytical methods available at that time. An investigation of available sampling and collection methodologies was performed, including the use of a glass loop or trap, silylated glass bulbs, and metal canisters. Based on these experiments, it was found that glass loops or traps was the best method to limit deposition of low volatility, high molecular weight species. Subsequent to this

study, improved sampling methodologies were developed (see for example Winer *et al.* 1989 and Arey *et al.* 1991a,b,c, and 1995). As discussed in section 4.6.1 of this report, these improved methodologies are recommended for any future emission rate measurements.

The inclusion of pertinent environmental conditions during the measurement process provided important information which, as discussed elsewhere, needs to be supplied with all emission rate measurements of this kind. As a result of reporting the original data, the emission rate factors obtained by these investigators can be re-adjusted to any given set of environmental conditions using the most current and reliable emission rate algorithms. As discussed in Section 4.8.4, a number of other investigations reporting emission rate factors in the literature did not specify the environmental conditions, instead supplying a value which had already been corrected to a given set of normalizing conditions. This practice makes it impossible to subsequently use a new correction algorithm to account for variable environmental conditions, thus imposing additional uncertainty in the compilation of biogenic inventories. However, one environmental parameter which was not adequately characterized in Winer *et al.* (1983) was light intensity. Since isoprene emissions are known to be highly dependent upon light intensity, this information should have been specified in greater detail than either "full" or "partial" sunlight. While it is likely that even partial sunlight was sufficient to provide for saturating conditions, reporting the precise level of solar insolation would have been preferable.

In their compilation of a total inventory, only two environmental conditions were assumed throughout the diurnal cycle (Winer *et al.* 1983). As noted above, daytime temperatures were assumed to be 30 °C with saturating light conditions, and nightime temperatures were maintained at 25 °C with no light available. This environmental protocol is now viewed as too simplistic since it does not accurately reflect normal diurnal variation, and is expected to introduce the greatest error in the early morning and late evening hours for isoprene emissions due to the lower light conditions prevailing at those times. Additional research is needed in order to obtain a better understanding of how isoprene emission rates change after dawn and before dusk for a representative set of plant species.

Another deficiency of this study, which was recognized by the authors, was the lack of measured emission rates from a given plant species at various times of the year, or at least at various times during the smog season. Measurements were only performed on either a single day

or over several days for a given plant species. This resulted in the emission rate being a "snap-shot" in time, not accounting for seasonal variability in emission rates, if any. While this problem has been encountered in most investigations of biogenic emission rates, it is a deficiency which needs to be addressed in any future studies.

Assignment of emission rate factors for unmeasured plant species based on measured plant species from the same genus was probably the best approach at the time of this study given the limited data in the literature. However, the lack of emission rate measurements for a substantial number of species within a given genus limited the reliability of these assigned values. Subsequent emission rate measurements for a substantial number of species has rendered the taxonomic approach more feasible although still with substantial ranges of uncertainty (Benjamin *et al.* 1996b). As a result, further development and testing of this methodology is recommended.

Overall, the work by Winer *et al.* (1983) was a comprehensive study which has served as a model for several subsequent investigations and whose data for leaf biomass and many emission rates are still being utilized. The procedures employed in this study can be recommended with some modifications, including the updated and improved methods for chamber sampling employed in later studies (Winer *et al.* 1989, 1992; Arey *et al.* 1991a,b,c, 1995), reporting of emission rates for each of the predominant monoterpene species emitted by a given plant species as well as any oxygenated organics emitted, and reporting of quantitative determinations of prevailing light intensity conditions during the measurement process.

4.10.2 Horie *et al.*, 1990, South Coast Air Basin

4.10.2.1 Overview of Emission Factor Development

This study was performed for the South Coast AQMD in an effort to build upon the investigation of Winer *et al.* (1983) with respect to compilation of leaf biomass and emission factors. The primary emphasis of this project, however, was placed on biomass distributions and the methodologies used to estimate these distributions (a review of this aspect of Horie *et al.* (1990) is provided in Section 3.5). These investigators did not perform direct measurement of emission rates from any plant species, but rather consulted the literature to compile a list of emission factors.

Horie *et al.* (1990) listed emission rate factors for each of the over 400 species identified by their investigation of the SoCAB. Each emission rate factor was normalized to standard conditions of 30 °C and full sunlight, and was listed in units of μg/g/hr. While not specifically stated, it is assumed that the units referred to μg hydrocarbon/g dry biomass/hr. Normalization to standard conditions was performed using the Tingey *et al.* (1979, 1980) environmental adjustment algorithms. Since only approximately 60 of the over 400 plant species listed had directly measured emission rates, emission rates had to be assigned to the remaining non-measured plant species. This was done using taxonomic relationships as described in Section 4.7 of this chapter first using genus level relationships, then by family level relationships. For a given plant species, assignment was made using the median value of all plant species of the same genus or family. For plant species for which an emission rate could not be assigned because no closely related species (at the genus or family level) had a directly measured value, an emission rate was assigned based on association by structural class. However, the details of how a given plant species was assigned an emission rate by this methodology was not disclosed.

4.10.2.2 Review of Emission Factor Development

The emission rate compilation by Horie *et al.* (1990) was similar to most other investigations up to that time. For example, all emission rate factors listed were normalized to standard conditions (30 °C and full sunlight) using the environmental adjustment algorithm developed by Tingey *et al.* (1979, 1980). All values for directly measured plant species listed in Horie *et al.* (1990) appear to be consistent with those listed in other studies up to that time. However, as discussed earlier, use of the Tingey *et al.* algorithms is out-dated and future inventories should use the algorithms developed by Guenther *et al.* (1993).

One problem associated with the emission factor development performed by Horie *et al.* (1990) concerned the assignment of emission rates based on structural class. It is currently uncertain whether this approach adds to or reduces overall biogenic inventory uncertainty. On one hand, assigning a non-zero emission rate to a plant species for which no related species have measured emission rates may provide a better estimate of actual total emissions than the practice of assigning no emission rate for those species as was done by Benjamin *et al.* (1996b). On the

other hand, this practice may result in an overestimation of emissions from a given plant species. At the present time, it is uncertain which of these two methods is best. Secondly, the assignment of which structural class a plant species belongs to is somewhat subjective, and can substantially influence total emission rates. In summary, assigning emission factors based on structural class may result in either an underestimate or an overestimate of true emissions. Further investigation of the use of structural class associations for the assignment of emission rates to plant species for which no closely related species has been directly measured is therefore needed.

One omission in the methodology of using structural class to assign emission rates was failure to state how the assigned value was determined. Since the median genus and family value was used to assign emission rates using the taxonomic method, it is assumed the median value of each structural class was also used. This however was not explicitely stated and is therefore unknown. Again, as stated earlier (Section 4.7), there currently exists insufficient data to determine whether use of the average value or median value is most appropriate.

There appeared to be a number of errors in the list of emission rate factors compiled by Horie *et al.* (1990). For example, even though both Joshua Tree (*Yucca brevifolia*) and Giant Yucca (*Yucca elephantipes*) were listed in the same structural class, they were assigned different emission rates. This type of inconsistency occurred many times throughout the emission factor list and the errors were not limited to structural class assignment.

4.10.3 Tanner *et al.*, 1991, San Joaquin Valley

4.10.3.1 Overview of Emission Factor Development

This study was performed in conjunction with the San Joaquin Valley Air Quality Study (SJVAQS) by the ARB and the Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX) funded by Pacific Gas and Electric, in order to provide an improved estimate of hydrocarbon emissions from biogenic sources for use in the Biogenic Model for Emission Estimation (BIOME) portion of Radian's Emissions Modeling System.

Emissions rate data were listed for a total of 138 individual species and vegetation types. Sources of these data included published literature, direct measurements performed by the authors of this study, and unpublished data from personal communications with other investigators. In

cases where no direct measurements had been performed or repeated for a given species, surrogate methodologies were applied to assign an emission rate.

Emissions rate data from direct measurements were compiled for 113 individual plant species prominent in the San Joaquin Valley air basin (SJVAB) and subdivided into 5 vegetation types: natural/shrubs/ornamentals (18 species listed), broadleaf trees (42 species), palms (3 species), conifers (24 species), and agricultural crops (26 species). In addition, three listings were given for multiple species. These were "7 hardwoods", "mixed hardwoods", and "irrigated pasture" as defined by Flyckt *et al.* (1980), Lamb (1985), and Winer *et al.* (1989), respectively.

Due to the prevalence of three particular vegetation species in the SJVAB and the lack of direct measurement of emission rates for these species, direct experimental measurements were made. The three tested species were Foothill (Digger) Pine (*Pinus sabiniana*), Blue Oak (*Quercas douglasii*), and Tarweed (a *Holocarphus* species). The procedure followed the method of Winer *et al.* (1989) and Arey *et al.* (1991). Isoprene measurements were conducted at three different times during the day (8-9 am, around noon, and mid-afternoon), corrected to 30 °C using the Tingey isoprene algorithm (Tingey *et al.*, 1979), and algebraically averaged. No reference was made concerning the levels of light intensity during the measurement procedures. Monoterpene measurements consisted of an additional measurement shortly after sunset, corrected to 30 °C using the Tingey terpene algorithm and averaged along with the daytime measurements.

For species where no direct measurements were available, surrogate emission rates were assigned based on taxonomic relationships. For this assignment, species of the same genus were considered first. If emission rates for species of the same genus were unavailable, species of the same family was used. Finally, if emission rates for species of the same family were unavailable, the authors assigned emission rates based on "educated guesses". Emission rate assignment was based on either a single related species or the average of two related species. In no case was the emission rate assignment based on more than two related species.

Emission rate data for non-agricultural species were expressed in units of μg hydrocarbon/g (dry biomass)/hr corrected to 30 °C and 1000 $\mu E/m^2/hr$ light intensity using the Tingey algorithms. No adjustments due to temperature or solar radiation were made for agricultural crops for which the applicability of the Tingey temperature algorithms was

questioned. Light intensity corrections were not made due to the lack of isoprene emissions from agricultural crops.

4.10.3.2 Review of Emission Factor Development

In listing emission factors from direct measurements reported in the literature, a bold zero was used by Tanner *et al.* (1991) to signify that the original study did not report any data for that category. However, consulting the original article, it was found that emission rates had often been quantified, but were below the detection limits for the apparatus used. This error often occurred when Tanner *et al.* cited data from Winer *et al.* (1983), and Winer *et al.* (1989). In total, a bold zero was assigned for 50 species for isoprene emission (36% of all species listed) and 27 species for terpene emission (20% of all species listed). If emission rates of zero had been properly assigned, a bold zero should have been applied to only 13 species for isoprene emission (9%) and 11 species for terpene emission (8%). As a result, there was actually less uncertainty in the data compiled by Tanner *et al.* than was implied by the assignment of a bold zero to plant species whose emissions were below the limits of detection.

Although the error described above will not affect the results of computer modeling simulations, the practice of setting an unknown emission rate to zero implies a conservative assumption which can, in principle, lead to an underestimation of vegatative emissions. Experimental detection limits might better serve as recommended emission rates, instead of assigning an unknown emission rate a value of zero. This would provide an upper limit estimate on the emission rate of a particular vegetative community.

For the experimental determination of emission rates for three plant species by Tanner *et al.* (1991), no reference was made concerning the light intensity present, although it was stated that the measurements took place at 8-9 am, near noon, and mid-afternoon (and shortly after sunset for the monoterpenes). This is insufficient information due to the possibility of clouds or haze during the measurement procedure resulting in reduced light intensity. Since isoprene emissions are known to be dependent on levels of light intensity, knowledge of these levels is critical.

The use of taxonomic relationships as applied by these investigators presents additional problems. When using genus or family level relationships to assign an emission rate, only one

or two members of that genus or family was used and the investigators failed to state how they decided which species to use. For example, why were certain related species disregarded and other used? It would have probably been better to use all members of the same genus or family rather than selecting one or two based on the investigator' best judgement. In addition, for species for which no direct measurements had been made for genus or family related species, assignments were made based on "educated guesses" by the authors. These assignment procedures diminish the reliability of the emission inventory. While the use of taxonomic relationships adds additional uncertainty to emission inventories, it appears to be the best methodology available at the present time. However, the practice of assigning emission rates based on the investigators' best judgement without providing rational for the selection of surrogate species is not recommended.